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USE OF CHEMILUMINESCENT
TECHNIQUES FOR THE
DETERMINATION OF OZONE AND
OXYGEN IN THE MARTIAN
ATMOSPHERE

This work performed for
Jet Propulsion Laboratories

Contract No. 950279

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SUMMARY

An investigation was carried out to determine the feasibility of a chemiluminescent detection system (rhodamine-B on silica gel) for use in measurement of ozone (and/or oxygen) in the Martian atmosphere.

Results indicate that such a device works well at pressures in the millimeter region, and provides a linear measurement of the mass flow rate of ozone through the instrument. Usable signals should be obtained at levels as low as 10^{-9} - 10^{-10} grams of ozone per minute.

Preparation of sensitive chemiluminescent discs is relatively simple and convenient. Once prepared, storage under anhydrous conditions is highly desirable.

If oxygen is excluded, the chemiluminescent discs are not affected by heating to 150°C for 24 hours. Thus, they will withstand pre-flight sterilization procedures.

Storage of discs under anhydrous conditions for about 3 months resulted in no deterioration of sensitivity. In fact, it generally improved their response, and tended to minimize sensitivity variations between the discs.

Temperature coefficients of freshly prepared discs are variable, probably due to varying moisture contents. However, dry storage also improves their behavior in this respect.

Disc sensitivities are approximately linear with temperature over the range -20°C to $+50^{\circ}\text{C}$ ($\sim 1\%$ per $^{\circ}\text{C}$ at 20°C). The useful temperature range of the instrument should extend over a range of at least -30°C to $+70^{\circ}\text{C}$.

Two different high-temperature photomultiplier tubes were evaluated, an ASCOP 543D and a CBS CL-1158. Neither gave as high a sensitivity as the Dumont 6467 normally used with the system. However it is believed that comparable sensitivities can be achieved by further development work.

No factor is presently anticipated, either in pre-flight procedures or during operation, which would render the chemiluminescent system undesirable for the contemplated mission.

The measurement of oxygen by the indirect procedure of UV - irradiation followed by ozone detection was briefly investigated. The response of the system is dependent on both the oxygen concentration and the total pressure. High sensitivities were achieved at atmospheric pressure (detection limit $\sim 0.01\%$ O_2). However, at pressures in the range 10 - 100 mm the low total pressure decreases the sensitivity of the method. More efficient dissociation of the oxygen than is currently achieved by the UV lamp would raise the overall sensitivity correspondingly.

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DETERMINATION OF OZONE

I. Introduction

The quantity and distribution of ozone in the Martian atmosphere would constitute an extremely interesting parameter for measurement. The CO_2 - CO - O - O_2 - O_3 system is postulated to play a large role in the photochemistry of the Martian atmosphere, and the equilibrium concentration of any one of these species is quite sensitive to the concentrations of the others. Thus, a measurement of the ozone profile should provide some insight as to a reasonable atmospheric model for this planet, both in terms of photochemical equilibria and planetary circulation.

Perhaps the most promising method of ozone measurement is the chemiluminescent system developed by Professor V. Regener at the University of New Mexico. Basically, the principle of the device is as follows: The gas to be monitored is aspirated past a surface which is coated with a chemiluminescent material (rhodamine-B adsorbed on silica gel). If ozone is present in the aspirated gas the surface glows due to an oxidation reaction. This glow is sensed by a photomultiplier tube, and the magnitude of the signal is taken as a measure of the ozone concentration.

Balloon sondes of this type are now being flown on a routine basis (by AFCRL) for determining ozone concentration profiles up to altitudes of 100,000 feet (11 millibars). Thus it is apparent that this device can function over the pressure range anticipated for the Martian experiment (10-100 mm). Indeed, Parametrics has just completed a flight with a modified sonde to a height of 132,000 feet (3 millibars) with good success.

As the feasibility of the chemiluminescent system for the detection of ozone in the Earth's atmosphere is well established, the objective of this program was to investigate what possible changes in design would be necessitated in order to accommodate the new environmental factors imposed by the mission under consideration. In particular, the final device must be able to withstand a pre-flight sterilization procedure consisting of heating to 150°C for a period of 24 hours. It must then remain "dormant" for a period of about six months during flight with no deterioration of response. Finally, it must operate in the Martian atmosphere at pressures ranging from 10 to 100 mm and over as wide a temperature range as possible.

Parametrics has just completed a contract with AFCRL, in which the effects of various parameters on the chemiluminescent system were studied, primarily in connection with its usage in balloon-borne meteorological sounding devices. Where pertinent, information developed in these studies has been included in this report so as to give a fuller picture of the characteristics of the method.

II. Experimental Methods

In general, the test systems used in the work described below all incorporated similar design features. First, an ozone source, in which a known concentration of ozone could be generated, followed by a reaction cell in which the chemiluminescent reaction took place. The light output was monitored by a photo-multiplier tube (Dumont 6467, unless otherwise specified)

operated at 1250 VDC (Fig. 1). The voltage drop across the 22M anode resistor was taken as a measure of the anode current, which in turn was proportional to the light emitted by the reaction.

A. Ozone Generation

In all cases, ozone was generated by the action of ultra-violet light (from a mercury discharge) on a stream of air or oxygen. When lamp intensity, irradiation geometry and gas composition are constant, a constant amount of ozone is generated per unit time. Therefore, the ozone concentration in the effluent gas will vary inversely with the flow rate past the lamp, thus affording a convenient means of varying the ozone content of the stream in a known fashion. Normally, the experimental ozone concentrations were established at relatively high flow rates ($\sim 1 - 5$ liters/min), and only a small fraction of this flow (0-300 ml/min) sampled by the reaction cell, the balance being vented. In this manner the flow rate through the cell could be varied without appreciably altering the flow rate past the lamp, and thus the ozone concentration,

For establishing relatively high ozone concentrations, the gas was passed over a "Pen-Ray" lamp (Type 11 SC-1, Ultra-Violet Products, Inc., San Gabriel, California) which was inserted directly into the gas stream as shown in Fig. 2. These lamps typically produce about 5×10^{-6} g (5 γ) of ozone per minute when irradiating air in this manner. For producing lower concentrations the gas stream was passed through a short (6") segment of quartz tubing, which was irradiated by a

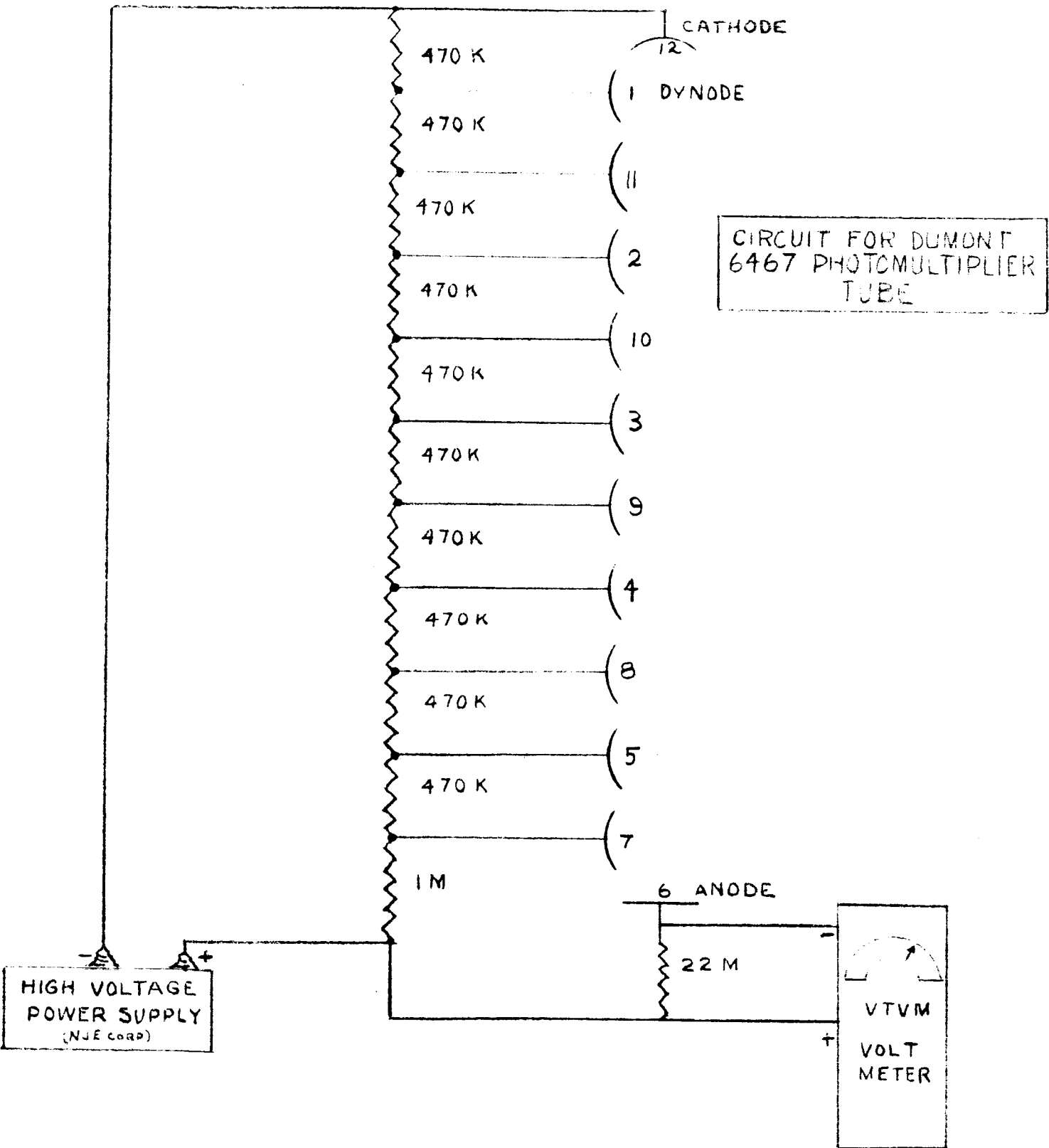


FIG 1

PEN LAMP OZONE GENERATOR

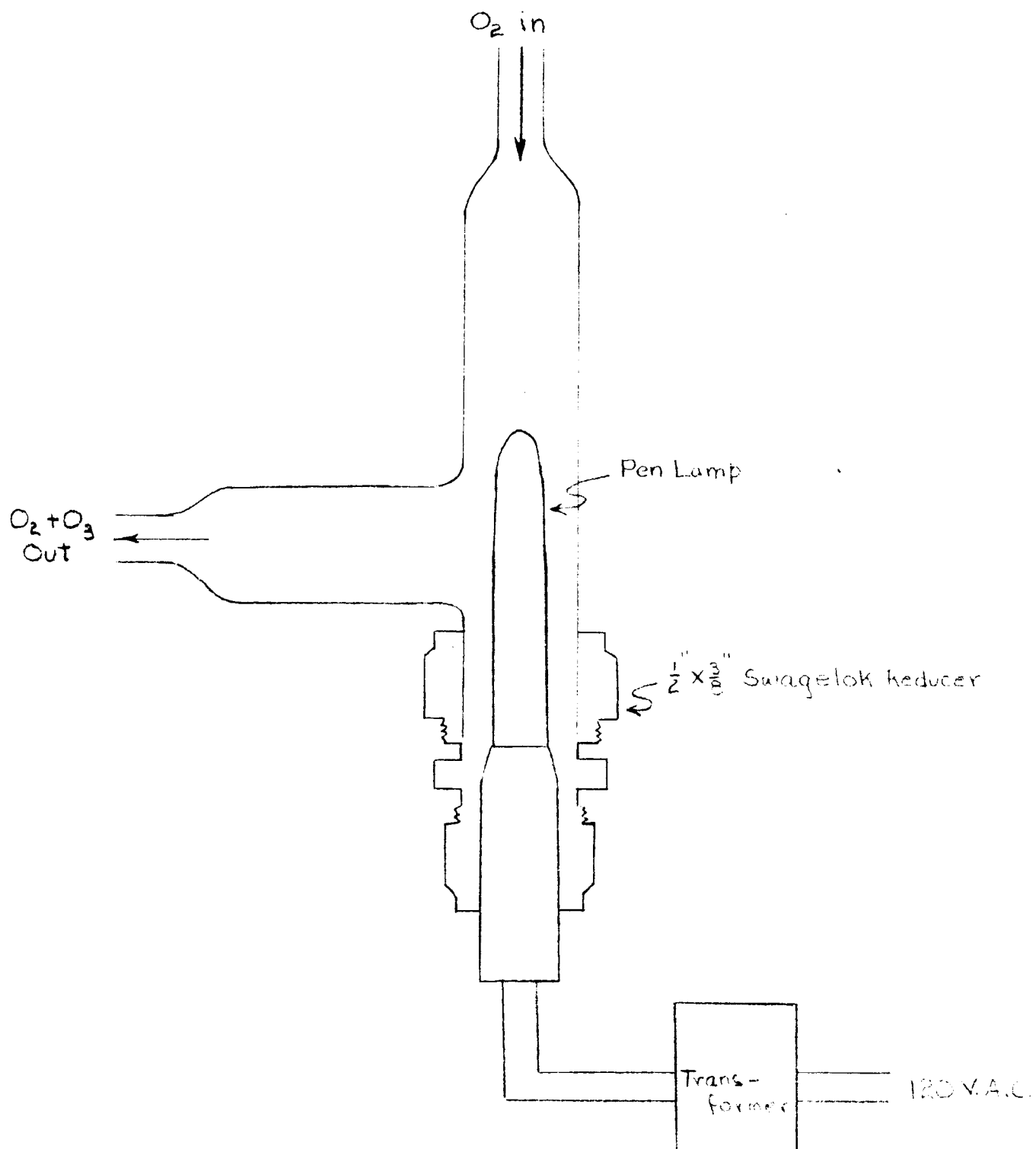


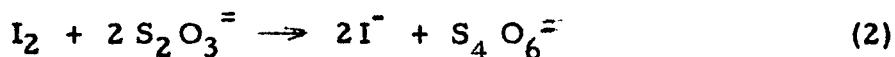
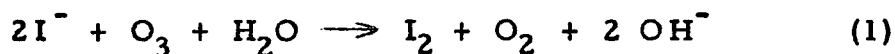
FIGURE 2

Hanovia SC 2537 lamp (Hanovia Chemical & Mfg., Co., Newark, N. J.) from a distance of about two inches. A typical production rate with this arrangement was about 0.1 γ ozone per minute, using pure oxygen and a lamp current of 5 ma.

B. Ozone Analyses

At the low concentrations in question, chemical determinations of ozone are rather tedious and time-consuming. In general most experiments were done on a relative basis, without a precise knowledge of the absolute ozone concentrations involved. However, calibrations of the ozone generators were made at regular intervals to insure against gross changes in ozone production due to such factors as lamp deterioration, gas line contamination, etc.

Ozone was determined by an indirect procedure utilizing the following reactions:



A stock solution was made up containing a known concentration of $\text{Na}_2\text{S}_2\text{O}_3$ and about 1% KI. The effluent from the ozone generator was then passed through a measured volume

of this solution for an appropriate length of time such that not all the $\text{S}_2\text{O}_3^{=}$ was reacted. The ozone in the gas stream reacted with the I^- according to equation (1), and the liberated I_2 immediately reacted according to reaction (2), the net result being to deplete the $\text{S}_2\text{O}_3^{=}$ in the solution. From the difference in $\text{S}_2\text{O}_3^{=}$ concentrations before and after bubbling, the total amount of ozone absorbed could then be calculated.

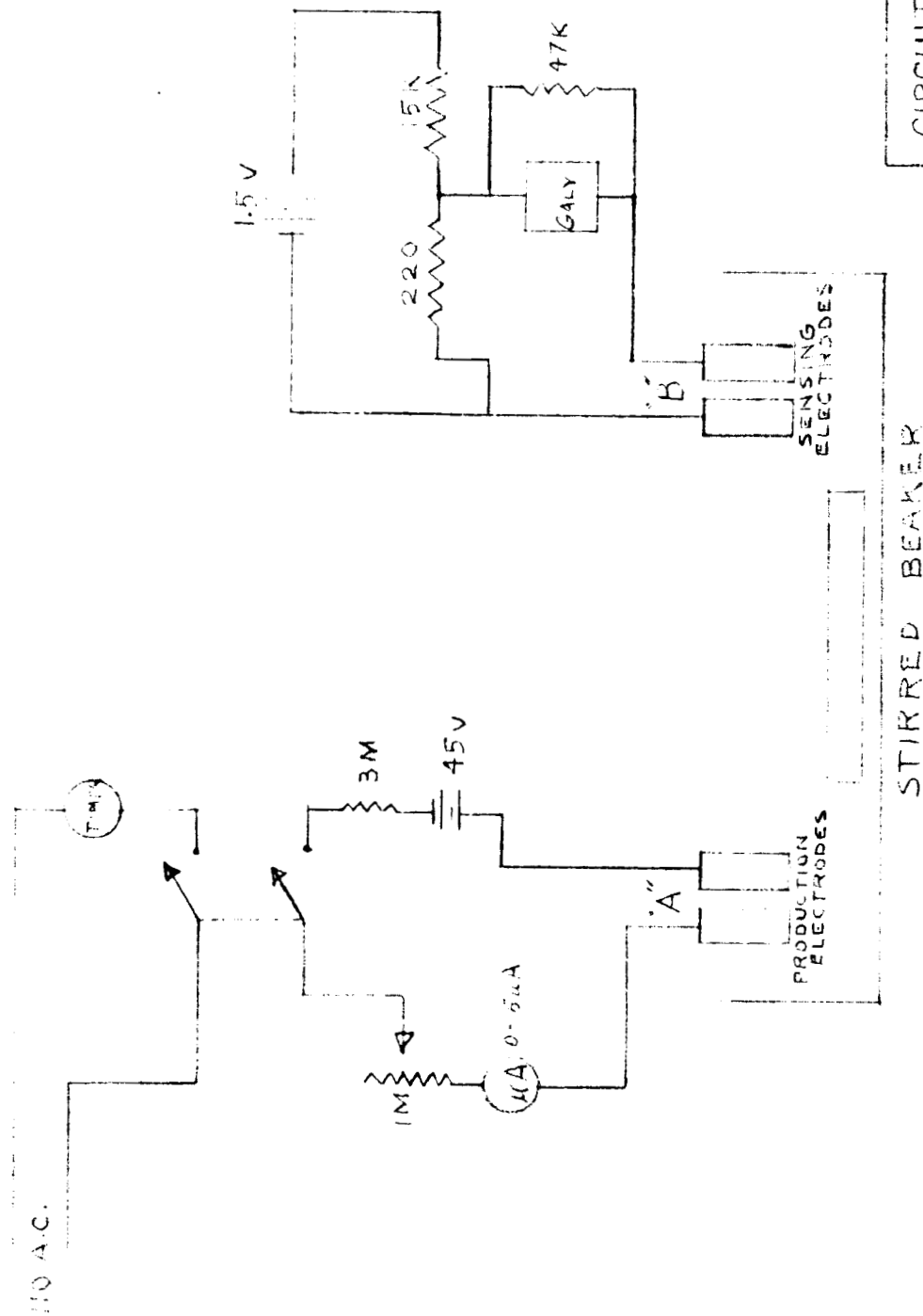
The concentrations of $\text{S}_2\text{O}_3^{=}$ in the solution (both before and after) were determined in the apparatus shown in Fig. 3. An aliquot of the solution was placed into the stirred beaker, in which were situated two sets of platinum electrodes. Set "A", the production electrodes, produced iodine electrolytically according to reaction (3a). Set "B", the sensing electrodes, were polarized to about 0.022 volts, and would pass no current until all the $\text{S}_2\text{O}_3^{=}$ had been destroyed and free I_2 appeared in solution. Current could then pass due to reactions (3a) at the anode and (3b) at the cathode, and the end-point was determined by observation of the galvanometer. From the production current and time, the total amount of iodine generated, and thus the concentration $\text{S}_2\text{O}_3^{=}$ in the solution, could be calculated from the equation:

$$N_{\text{thio}} = \frac{10^3 \times i \times t}{96,500 \times V_a}$$

where

$$N_{\text{thio}} = \text{normality of } \text{S}_2\text{O}_3^{=}$$

FIG. 3



CIRCUITRY FOR
THIOSULFATE
DETERMINATION

- i = production current (amperes)
- t = production time (seconds)
- V_a = volume of solution taken (ml) for analysis
- V_T = total volume of solution in bubbler (ml)

C. Reaction Cells

Several reaction cells were used, slight design modifications being made in each (water jackets, etc.) to facilitate the study of various parameters. However, they all consisted of a photomultiplier tube mounted with its window in close proximity to and directly facing a chemiluminescent disc (see section D.). A gas inlet and outlet were provided so as to achieve a reasonably symmetric flow of the gas over the face of the disc. A typical cell is shown in Fig. 4, which depicts the reaction cell used in the low-pressure and flow-rate dependence studies.

D. Chemiluminescent Discs

Except where otherwise noted, the chemiluminescent discs referred to in this report were made by depositing the active material on circular aluminum planchets $1\frac{1}{4}$ " diam. $\frac{3}{32}$ " deep. This size was chosen to match the diameter of the photomultiplier tubes.

The active material could be made and coated onto the disc by several procedures, with only slight variations in the final response of the disc. The variations found between discs

REACTION CELL

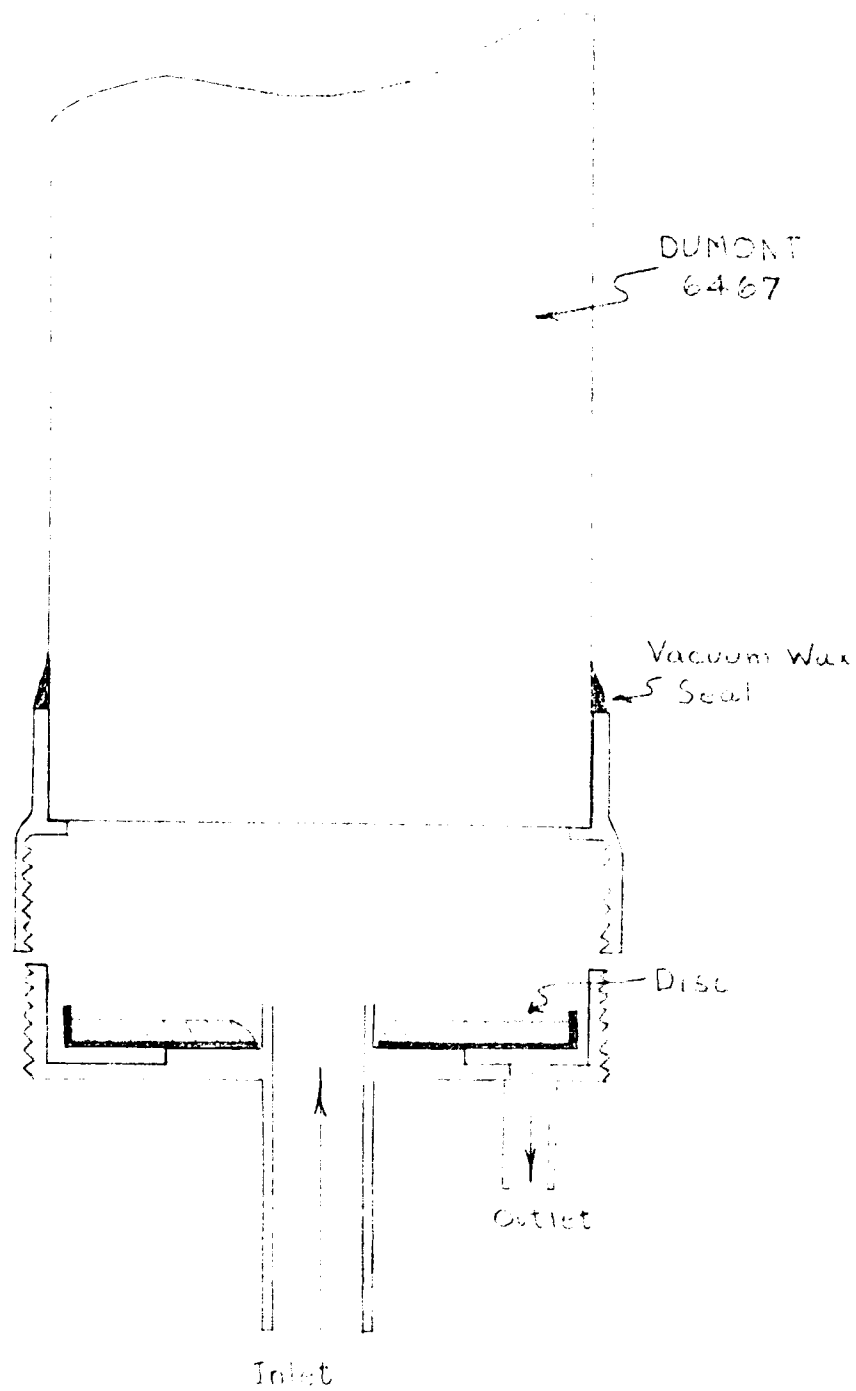


FIG 4

prepared in the same manner were as great as the variations found between discs prepared in different manners. Indeed, although a good deal of effort was expended in attempting to optimize preparative procedures, no quantitative correlations could be made in this area. Presented below is the most convenient preparative procedure:

About 1 mg of rhodamine B dye was dissolved in 50 ml of acetone. To this solution 3 g. of silica gel (either Davison mesh 28-200 or Impalpable Powder) was added. The adsorption of the dye onto the silica gel was quite rapid, the solution becoming noticeably decolorized. The silica gel was then filtered and allowed to dry.

To deposit a coating of this material on a metal surface, a drop of "Duco" cement (cellulose nitrate base) was added to a slurry of the gel in acetone. The slurry was then deposited on the metal surface and allowed to dry. The resultant coatings proved rugged enough for normal laboratory usage, although with the coarser mesh gel there was a tendency to form a rigid surface crust, below which the material remained relatively loose.

In an attempt to attain more uniform coatings a batch of 100 discs was also coated with the rhodamine-gel (impalpable powder) by electrophoretic deposition. This was performed commercially by Indelco, Inc., Beverly, Mass. In this process, the semi-colloidal gel particles are suspended in an inert solvent, given electrical charges by small quantities of adsorbed ions, and then made to deposit onto a metal substrate by applying an

electric field. For mechanical stability a small amount of binder (carbowax) is added to the solvent. These electrophoretically coated discs were used for the bulk of the work reported below.

III. Results

A. Low-Pressure Experiments

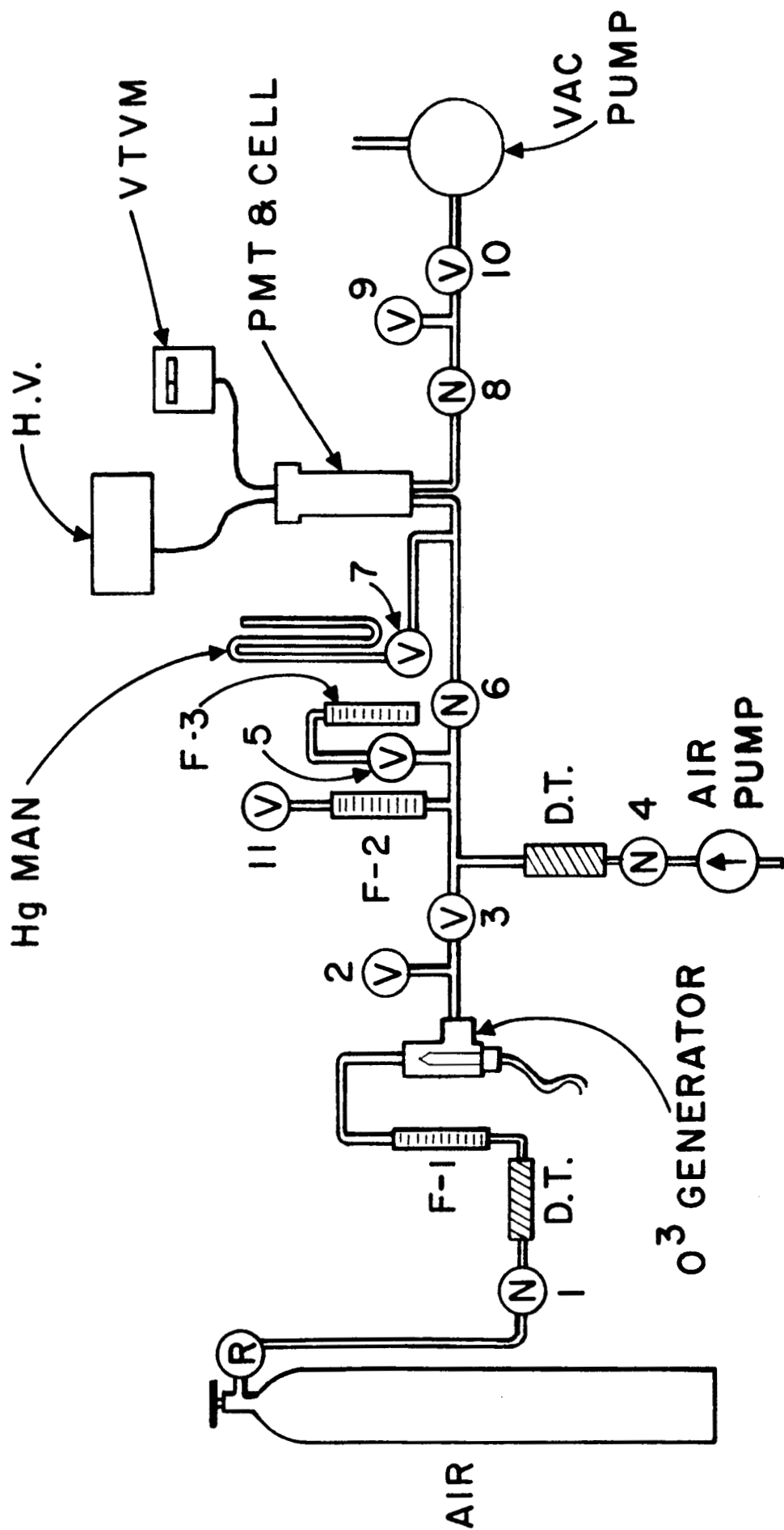
In order to ascertain the dependence of the signal on ozone concentration, pressure, and gas flow rate, the system shown in Fig. 5 was constructed. The reaction cell is shown in Fig. 4. It consisted of a two-piece brass housing which fit over the head of a Dumont 6467 photomultiplier tube. A center hole was drilled in the chemiluminescent discs so as to seat over the intake tube as shown.

The response of the system was measured at pressures ranging from 5 mm to 170 mm, flow rates from 130 ml/min to 1 liter/min, and at ozone concentrations from 0.007 $\mu\text{g/liter}$ to 0.7 $\mu\text{g/liter}$. Over these ranges, the signal appeared to be linearly dependent on the ozone flux passing through the reaction cell, i. e., the product of ozone concentration and gas flow rate. Typical data are shown in Figs. 6 and 7. In these figures, F_c denotes the flow rate through the cell, P_c the pressure in the cell, and J is the ozone flux through the cell in $\mu\text{g/minute}$. F_c and J were calculated from

$$F_c = F'_c \times \frac{P_{\text{atm}}}{P_c}$$

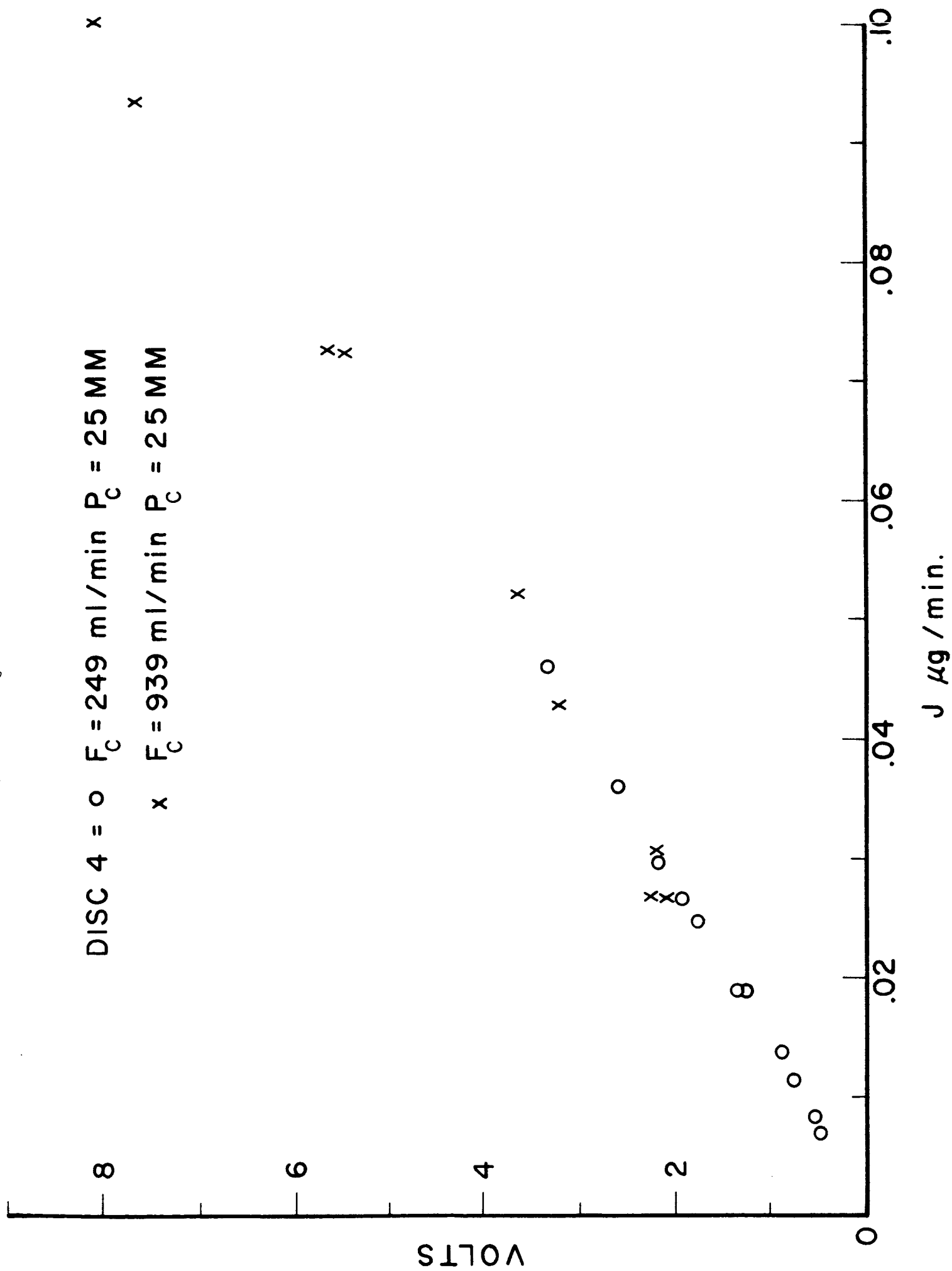
$$J = R_L \times \frac{F'_c}{F_T}$$

FIG 5



DISC 4 = o $F_c = 249 \text{ ml/min}$ $P_c = 25 \text{ MM}$

x $F_c = 939 \text{ ml/min}$ $P_c = 25 \text{ MM}$



DISC 4 - \circ $F_C = 946 \text{ ml/min}$; $P_C = 25 \text{ mm}$
 Δ $F_C = 614 \text{ ml/min}$; $P_C = 38.5 \text{ mm}$
 \square $F_C = 132 \text{ ml/min}$; $P_C = 171 \text{ mm}$

VOLTS

$J \mu\text{g/min}$

0.2 0.4 0.6 0.8 1.0

8

6

4

2

0

\circ 8 Δ

8 Δ

8 Δ

8

8 Δ

\circ Δ

where

F_C' = flow rate through cell at atmospheric pressure
(from flow meter F_3)

R_L = rate of ozone production of UV lamp ($\mu\text{g}/\text{min}$)

F_T = flow rate of gas past UV lamp + flow rate of
diluting air F_2 .

Note the reproducibility and linearity of the points, despite the wide variations in pressure, flow rate, and concentration.

B. Concentration and Flow-Rate Dependence at Atmospheric Pressure

A short corollary experiment was performed in the apparatus shown in Fig. 8, in which the effects of ozone concentration and flow rate were investigated at atmospheric pressure. In this set-up, the ozone concentration could be varied by varying the gas flow rate past the UV lamp; i. e. , the concentration was inversely proportional to F_L , as explained previously. The flow rate through the cell was controlled by a needle valve placed in front of a small pressure vacuum type air pump, and this flow rate was read from a flow meter connected to the outlet port of the pump.

Figure 9 shows the linear dependence of the signal on relative ozone concentration at a constant flow rate through the cell of 300 cc/min.

FIG. 8

SYSTEM FOR STUDYING FLOW-RATE DEPENDENCE

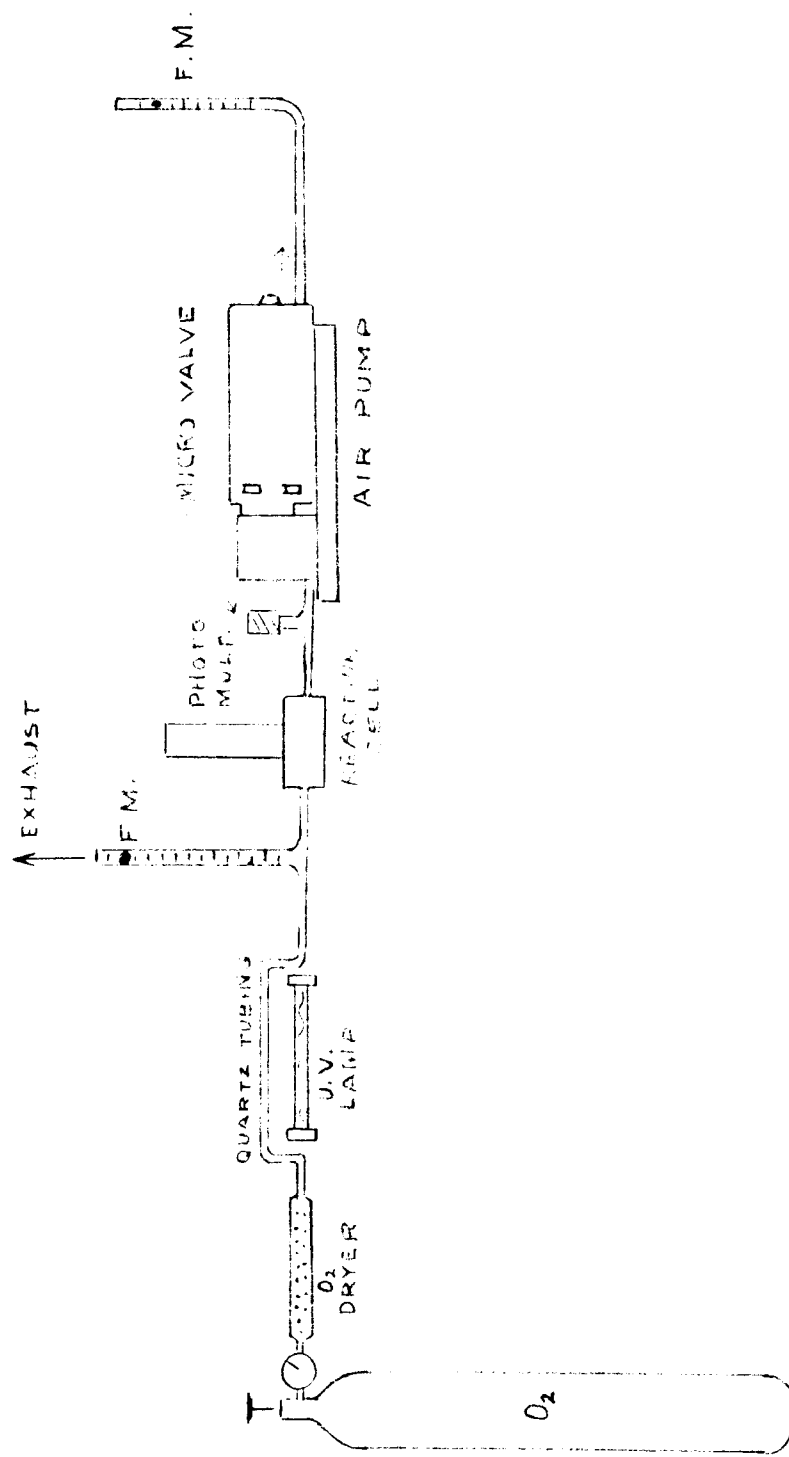
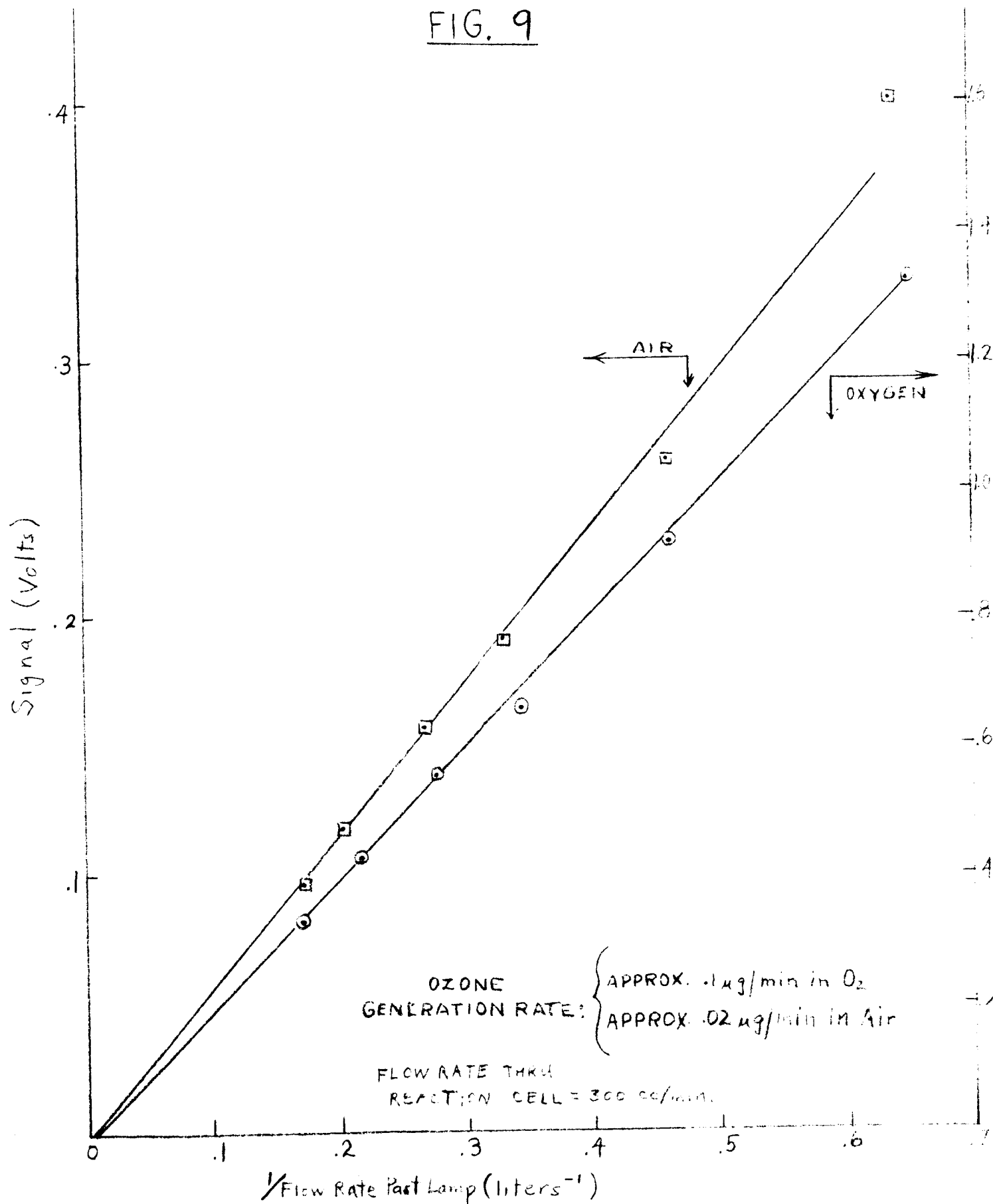


FIG. 9



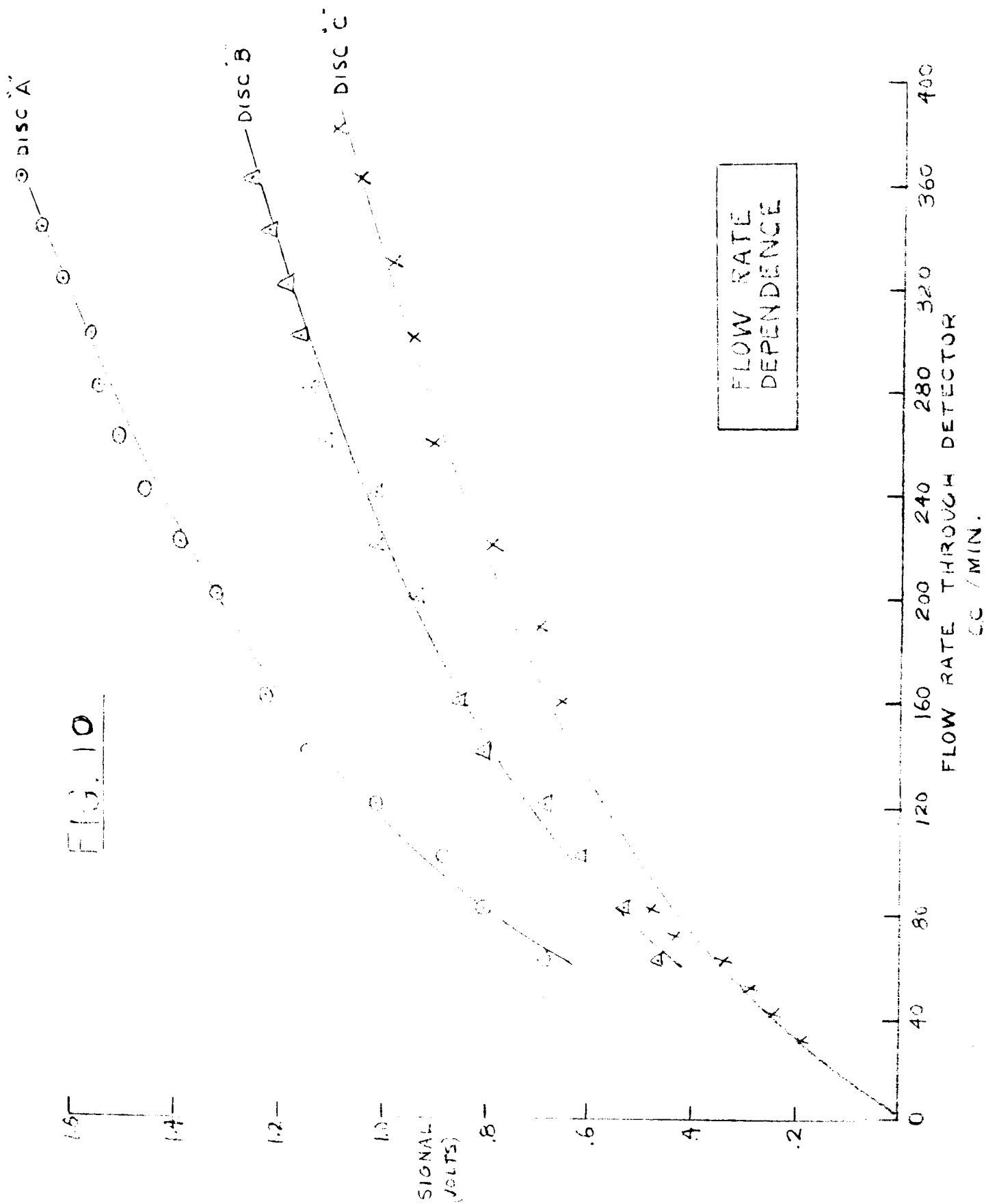
At a constant ozone concentration, however, the signal was found to deviate from linear dependence on the flow rate, as shown in Fig. 10. This deviation seemed to occur at flow rates higher than about 150 cc/min. This behavior was in marked contrast to the flow-rate dependence at lower pressures where linearity was preserved up to 1 l/min in some cases. It appears, therefore, that this effect should cause no serious problems at the ambient Martian pressures.

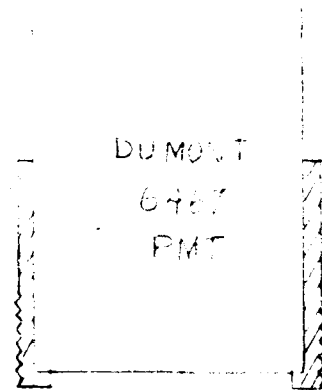
C. Temperature Dependence

In order to investigate the temperature dependence of the rhodamine-silica gel discs, the jacketed brass reaction cell shown in Fig. 11 was constructed. The temperature of the cell was determined by circulating liquid through the jacket from a constant temperature bath. The jacket temperature was monitored by a thermometer placed in the effluent liquid line. The flow of ozonized gas through the cell could be stopped and started at will by operating a manually controlled solenoid valve located at the exit port, and the gas flow rate was set by the exit orifice located immediately downstream from the solenoid. This orifice was adjusted so as to give a flow rate of 300 cc/min, comparable to that achieved by the reciprocating bellows pump used in the present ozone sonde.

Temperature coefficients were determined by having the discs sample a constant ozone concentration, and measuring the output signals as a function of disc temperature. As with sensitivity to ozone, these coefficients varied from disc to disc. However, it is interesting to note that discs which were stored

FIG. 10





CELL FOR
TEMPERATURE
STUDIES

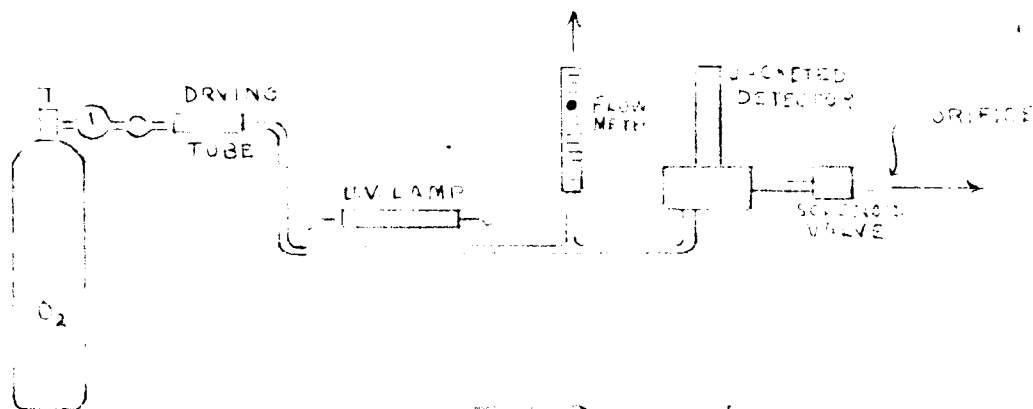
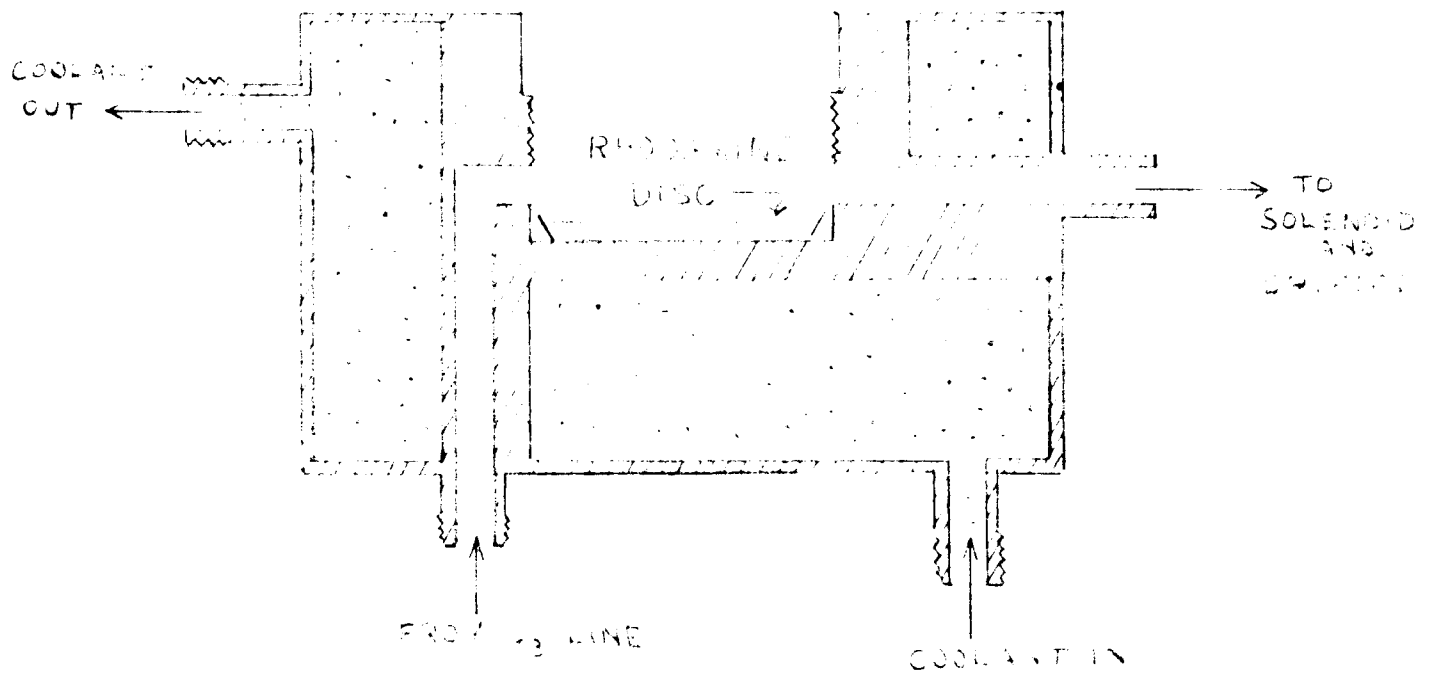


FIG. 11

for a time under anhydrous conditions (see section D) had lower and more reproducible temperature coefficients. Figure 12 shows the data taken with one such disc. This disc had been stored several weeks before use in a dessicator over P_2O_5 . Note that the curvature at high temperature is an artifact introduced by the temperature characteristics of the photomultiplier tube. To correct for this, a calibration was made of photomultiplier signal vs. temperature, with no disc in the reaction cell, but with a lamp mounted externally in such a way as to result in a constant light "leak." On the basis of this calibration (shown in Fig. 13) the previous data at higher temperatures was corrected, with the results shown as the dotted line in Fig. 12. Figure 14 shows data taken with a freshly made disc, indicating the large magnitude of some of the temperature coefficients which have been measured.

D. Sterilization and Storage

1. Chemiluminescent Discs - A group of 75 discs was set aside for a study of their response to sterilization at $150^{\circ}C$ followed by long-term storage under various conditions. Sterilization conditions were approximated by heating the discs to $150 - 160^{\circ}C$ in a laboratory oven. Laboratory dessicators, either evacuated or containing nitrogen, oxygen or air, were used as storage containers. These containers were kept either anhydrous (by the use of P_2O_5), or moist (by using saturated salt solutions). Some discs were stored for a time, and then sterilized, while others were sterilized first, and then stored. Samples from each batch were periodically checked for response to ozone.

FIG 12

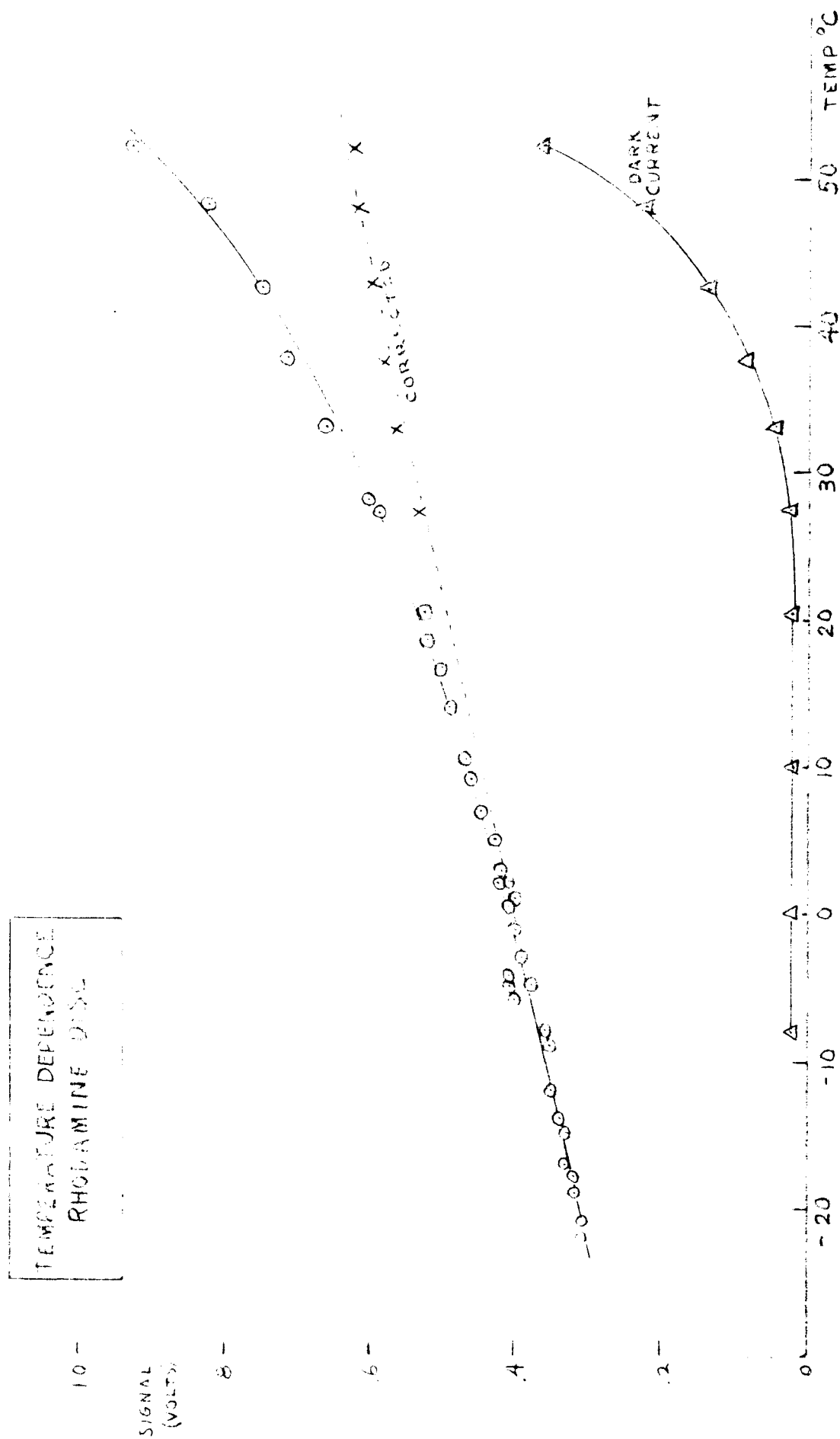


FIG. 13

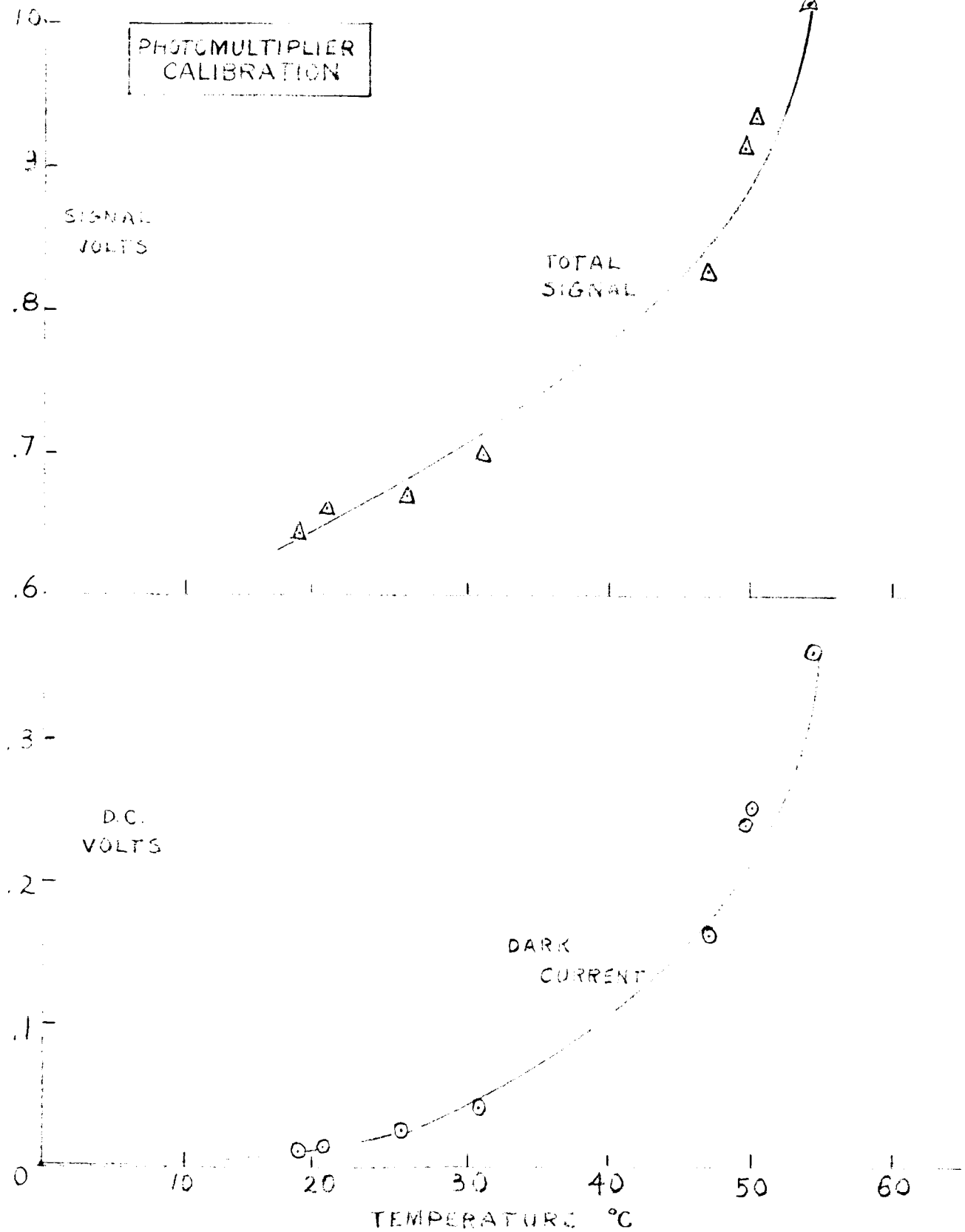
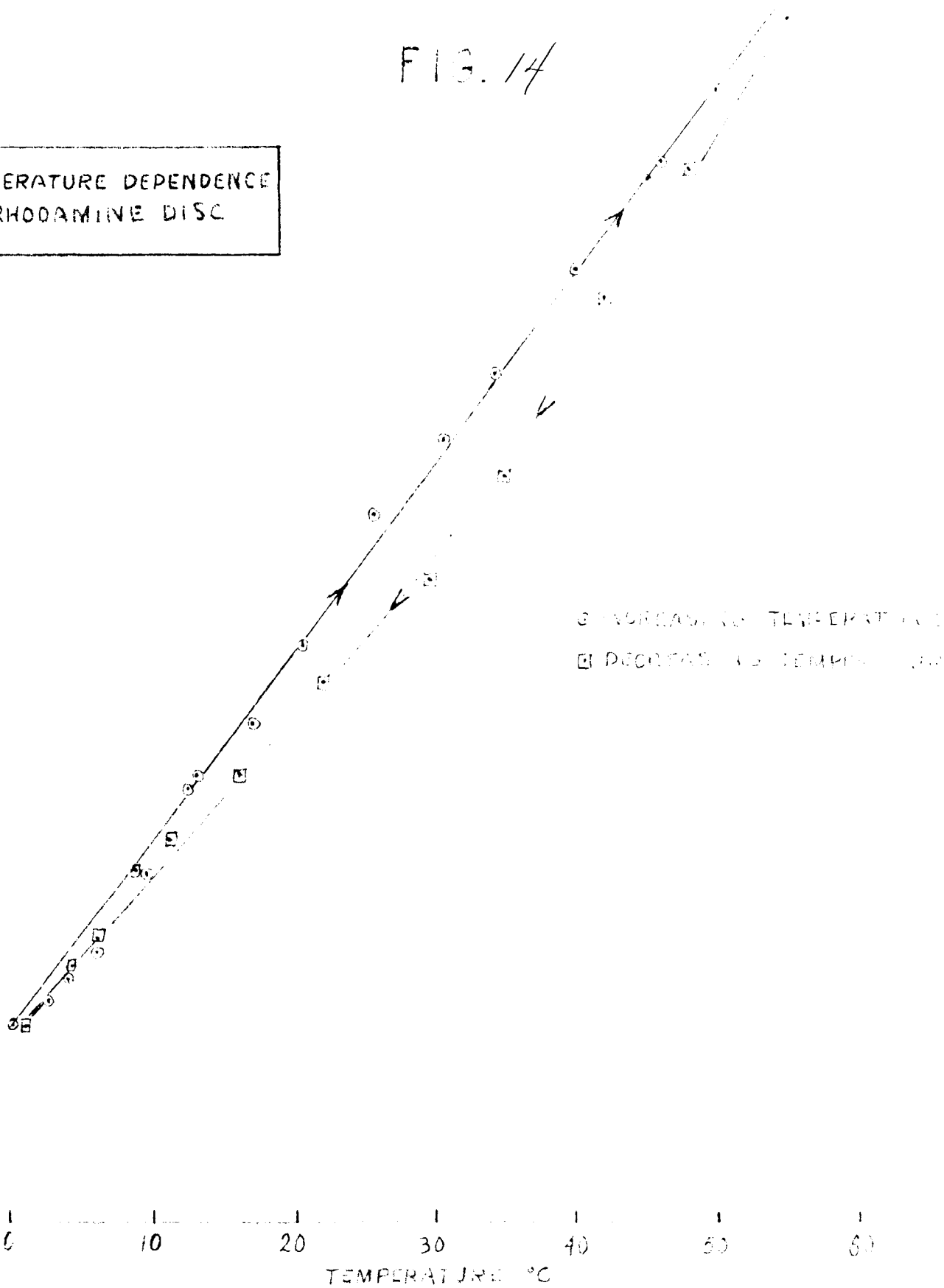


FIG. 14

TEMPERATURE DEPENDENCE
RHODAMINE DISC



The results of these experiments indicated which procedures were markedly deleterious to the discs. However, due to variations in disc response, even among those subjected to identical procedures, it was not possible to differentiate between the "safe" procedures with any confidence.

Heating the discs to 150°C in air resulted in complete loss of sensitivity to ozone. This was accompanied by marked discoloration of the discs, indicating oxidation of the organic dye. If the discs were heated in an argon atmosphere, however, they emerged essentially unchanged. Apparently, then, the sterilization procedure will not result in deterioration of the discs so long as oxygen is excluded from the system during the treatment.

With respect to storage, the only obvious restriction is that the discs be stored under anhydrous conditions. Storage at 80% relative humidity (room temperature) resulted in immediate deterioration of the ozone sensitivity, even after only several hours. Some of this deterioration was apparently reversible, as the signal tended to build up when the disc sampled the (dry) gas from the ozone generator for extended periods of time.

The atmosphere under which the discs were stored, whether vacuum, argon, oxygen or air, seemed to have no particular effect on disc sensitivity, so long as anhydrous conditions were maintained. In fact, general improvement, both in sensitivity and temperature coefficient (see section C) were obtained upon prolonged storage in a dry environment.

In the time available, it was not possible to duplicate the contemplated six months dormancy. However, the fact that under proper conditions, the discs could be successfully stored for about 3 months with no drastic reduction in sensitivity, indicates that the aspect should present no great problem.

2. Other Components - No other components of the system were actually subjected to the sterilization procedure. However, two "high-temperature" photomultiplier tubes were obtained; an Ascop 543D and a CBS CL-1158. Both these tubes are claimed to withstand high-temperature treatment, and in fact, to operate at high temperatures, the Ascop to 150°C and the CBS to 125°C.

In order to estimate the sensitivities of these tubes to the rhodamine-B luminescence, a new reaction cell had to be built, as both tubes are 2" in diameter, as compared to $1\frac{1}{4}$ " for the Dumont 6467 used in our other studies.

Direct quantitative comparisons of the high-temperature tubes with the Dumont 6467 was difficult, as the use of a new reaction cell introduced uncertainties in other parameters, such as gas flow characteristics, optical coupling between phototube and disc, etc. For example, one could attempt a comparison using the same disc and the same ozone concentration. However, this would entail placing a $1\frac{1}{4}$ " disc in a 2" holder, thus severely changing the geometry of the reaction cell. On the other hand, one could make a 2" disc to use with the high-temperature tubes, but would then be unable to use it with

the $1\frac{1}{4}$ " Dumont tube. Also bearing on this problem is the arbitrariness of the electrical parameters used. The 1250 volts applied to the Dumont tubes, together with the 22 M anode resistor, were chosen mainly as a matter of convenience, as these values gave easily measurable (with a vacuum-tube voltmeter) output signals in the ozone concentration range of interest (0.01 - 0.5 $\mu\text{g/liter}$). However, the gain vs. voltage/stage curves for different types of photomultiplier tubes may be quite different, and there are differences even between tubes of the same type. Thus it is not very meaningful to compare the absolute values of the signals developed across the anode resistors. One may attempt to normalize the situation by adjusting conditions so as to give equal "dark currents," and then take the absolute signals developed as a measure of signal/noise ratio. This is not strictly rigorous, however, as the "dark current" is not really "noise," and may be very stable indeed.

The procedure which was used in comparing the high-temperature phototubes was to adjust the voltage per stage so as to give approximately the same "dark current" signal across the (22 M) anode resistor as was obtained with the Dumont tubes (approximately 0.04 volts). A 2" chemiluminescent disc was placed in the new reaction cell and monitored by the phototubes while sampling a concentration of 0.10 $\mu\text{g O}_3/\text{liter}$ at a flow rate of 300 cc/min. Whereas the Dumont tubes (with $1\frac{1}{4}$ " discs) normally give a signal of several volts under these conditions, the CBS tube gave a signal of only 0.3 volts, and the Ascop tube practically no signal at all (~ 0.01).

IV. Discussion and Conclusions

A. Disc Preparation and Storage

It is apparent that there are still many uncontrolled parameters associated with the preparation of the chemiluminescent discs. The variability in sensitivity between discs, even those prepared from the same batch of dyed silica gel, is indicative of this fact. Associated experiments have led us to believe that the sensitivity of a given disc is a complex function of its past history; in particular, its past exposure to moisture appears to be quite important. The deleterious effect noted on sensitivity of storing the discs at 80% RH, is but one indication of this. The improvement in sensitivity upon storage under anhydrous conditions is also obviously associated with the loss of water from the gel.

Although control procedures are relatively loose in the preparation process, it would probably not be worthwhile at present to devote a large effort to establishing extremely rigid procedures in order to produce "optimum" discs having minimum variation in sensitivity. Present procedures are able to produce large numbers of discs having quite adequate sensitivities, all falling within less than an order of magnitude of each other. If necessary, a selection procedure may be employed to pick those of highest sensitivity for the limited quantities which will be needed.

Storage of the discs under anhydrous conditions appears to be the only prerequisite for long-term retention of sensitivity. Indeed, a dry environment apparently is beneficial.

When employing these discs in terrestrial meteorological applications, pre-flight calibration, as near as possible to the actual time of launch is highly desirable for accurate interpretation of the flight data. In the case of the proposed Martian experiment, the 6-month interval may present some problems if highly accurate information is desired. In this case, some sort of in-flight, pre-encounter, calibration may be called for. However, the long-term sensitivity "drift" of the discs is not very great (50% in the worst case) and if only order-of-magnitude information is desired, we foresee no difficulty in calibrating before launch. It should be pointed out that even if information as to the absolute ozone concentrations is ambiguous due to possible sensitivity changes, the shape of the measured vertical ozone profile will still be quite valid and accurate.

B. Pumping

The results of the low-pressure experiments indicate that the chemiluminescent detector is indeed a true ozone mass sensor, responding linearly to the total amount of ozone per unit time passing through the cell. Thus, in order to exactly determine the ozone concentration (e. g., $\mu\text{g/liter}$), the volumetric flow rate through the cell must be fixed. This is the purpose of the reciprocating bellows pump on the ozone sonde, which expands to a constant volume regardless of the ambient pressure. This arrangement works quite well in balloon-borne sondes even at pressures as low as 2-3 mm Hg.

One point which should be noted, in connection with experience gathered from balloon flights, is the behavior of the device after the balloon has burst. Although the units are fitted with small parachutes, these are usually not very effective at high altitudes and the rate of fall is quite high. In these cases, the apparent ozone concentrations measured during the descent are appreciably higher than those measured during the relatively slow ascent. This may be explained on the basis of a "self-pumping" phenomenon whereby the rapid rate of increase in ambient external pressure leads to a net flow of gas into the bellows. In the contemplated Martian experiment, therefore, the rate of increase in ambient pressure as the package drops through the atmosphere should be carefully considered. Indeed, if this is high enough, the pump might be dispensed with entirely. If pressure and temperature sensors are included, the instantaneous volumetric flow rate could be readily calculated as shown below:

Consider a package consisting of a "ballast volume" initially evacuated, connected to the external environment by means of an inlet tube. (For this discussion, assume the ozone reaction cell is part of the inlet tube.) As the package falls through an atmosphere of increasing density, the pressure inside this volume tends to equilibrate with the external pressure, thus leading to a net flow of gas into the volume through the inlet tube:

$$\frac{dn_i}{dt} = \frac{V_i}{RT_i} \frac{dP_i}{dt} \quad (1)$$

where

n_i = moles of gas inside the volume

V_i = ballast volume

T_i = gas temperature inside the volume

P_i = pressure inside the volume

R = gas constant

t = time

This influx of gas corresponds to an equivalent volumetric flow rate (as measured at the ambient external pressure)

$$\frac{dn_i}{dt} = - \frac{dn_a}{dt} = - \frac{P_a}{RT_a} \frac{dV_a}{dt} \quad (2)$$

$$- \frac{dV_a}{dt} = \frac{RT_a}{P_a} \frac{dn_i}{dt} = \frac{T_a}{T_i} \frac{V_i}{P_a} \frac{dP_i}{dt} \quad (3)$$

where

n_a = moles of gas external to ballast volume

$$\frac{dV_a}{dt} = \text{equivalent volumetric flow rate into ballast volume (measured at } P_a)$$

$$T_a = \text{external gas temperature}$$

$$P_a = \text{external gas pressure}$$

Thus by monitoring internal and external temperatures, and pressures, it is possible to calculate the flow rate through the ozone reaction chamber.

It is of interest to follow this concept one step further, and derive an expression by which one may estimate the flow rates attainable from various meteorological and vehicle parameters:

Let h = altitude

P_a = ambient atmospheric density

ρ_i = gas density inside ballast volume

Assume: (a) The rate of fall through the atmosphere is constant;

$$-\frac{dh}{dt} = F; \quad h = H - Ft \quad (4)$$

(b) The ambient atmospheric density is approximately exponential with altitude;

$$\rho_a = A e^{-Kh} \quad (5)$$

$$\frac{d\rho_a}{dt} = -K A e^{-Kh} \left(\frac{dh}{dt} \right) = F K \rho_a \quad (6)$$

- (c) The conductance of the inlet tube is high enough so that the gas in the ballast volume is always in equilibrium with the ambient atmosphere;

$$P_i = P_a \left(\frac{T_i}{T_a} \right)^{1/2} \quad (7)$$

low pressures (molecular flow region)

or

$$P_i = P_a \quad (8)$$

at higher pressures (viscous flow region)

- (d) The internal temperature of the ballast volume does not change appreciably during the experiment:

$$T_i = \text{constant}$$

- (e) The ambient atmospheric temperature may be approximated by a linear function of altitude:

$$T_a = T_o + Qh \quad (9)$$

$$\frac{dT_a}{dt} = Q \frac{dh}{dt} = -QF \quad (10)$$

From (3)

$$\text{flow rate} = \frac{-dV_a}{dt} = \left(\frac{T_a}{T_i} \right) \left(\frac{V_i}{P_a} \right) \left(\frac{dP_i}{dt} \right)$$

For molecular flow conditions:

$$\begin{aligned}
 \frac{dP_i}{dt} &= T_i^{1/2} \frac{d}{dt} \left(\frac{P_a}{T_a^{1/2}} \right) \\
 &= T_i^{1/2} \left[T_a^{-1/2} \frac{dP_a}{dt} - \frac{1}{2} P_a T_a^{-3/2} \frac{dT_a}{dt} \right] \\
 &= \frac{T_i^{1/2}}{2 T_a^{3/2}} P_a \text{ OF} + \frac{T_i^{1/2}}{T_a^{1/2}} \frac{dP_a}{dt} \quad (11)
 \end{aligned}$$

However

$$P_a = \frac{\rho_a R T_a}{M} \quad (12)$$

where M = average molecular weight

Therefore

$$\frac{dP_a}{dt} = \frac{R}{M} \frac{d}{dt} (\rho_a T_a)$$

$$\begin{aligned}
&= \frac{R}{M} \left[-\rho_a QF + T_a FK \rho_a \right] \\
&= P_a F \left[K - \frac{Q}{T_a} \right] \quad (13)
\end{aligned}$$

Therefore:

$$\begin{aligned}
\frac{dP_i}{dt} &= \frac{T_i^{1/2}}{2T_a^{3/2}} (FQ P_a) + \frac{T_i^{1/2}}{T_a^{1/2}} P_a F \left(K - \frac{Q}{T_a} \right) \\
&= \frac{FP_a T_i^{1/2}}{T_a^{1/2}} \left[\frac{Q}{2T_a} + K - \frac{Q}{T_a} \right] \\
&= \frac{FP_a T_i^{1/2}}{T_a^{1/2}} \left[K - \frac{Q}{2T_a} \right] \quad (14)
\end{aligned}$$

and

$$\text{Flow Rate} = -\frac{dV_a}{dt} = \left(\frac{T_a}{T_i} \right) \left(\frac{V_i}{P_a} \right) \left[\frac{FP_a T_i^{1/2}}{T_a^{1/2}} \left(K - \frac{Q}{2T_a} \right) \right]$$

$$\text{Flow Rate} = \frac{V_i F}{(T_a T_i)^{1/2}} \left(K T_a - \frac{Q}{2} \right) \quad (15)$$

By analogous means it can be shown that for viscous flow:

$$\text{Flow Rate} = \frac{V_i F}{T_i} (K T_a - Q) \quad (16)$$

C. Temperature Dependence

The temperature response of most discs measured was relatively linear in the range -20°C to 50°C , the rate of change with temperature being about 1% per degree at 25°C . Measurements below -20°C were not achievable in the apparatus used, and those above 50°C were not possible due to the excessive dark current of the Dumont phototube.

The temperature dependence of the ozone response like the disc sensitivity, appears to be a function of the particular disc being studied. In addition, there are indications that it is also a function of the flow rate of gas through the reaction cell. Unfortunately, not enough time was available to study temperature dependencies at low pressures, as it is felt that there is a strong possibility that the temperature coefficients at low pressure might be appreciably lower than those measured at atmospheric pressure.

An interpretation of the temperature dependence of this phenomenon is complicated by the uncertainty as to its mechanism. However, we may generally describe the chemiluminescent process as follows:

- (a) ozone diffuses to the substrate,
- (b) ozone is adsorbed onto the substrate,
- (c) the ozone reacts with a substrate species,

(d) the energy of this reaction is transferred to a luminescent center electronically exciting a rhodamine-B molecule,

(e) the rhodamine-B fluoresces, emitting light.

All of these processes are probably temperature-dependent, some much more so than others. The actual measured temperature-dependence of the process will be a function of the complex interplay between them.

In general, processes (a), (b) and (c) should occur more rapidly as the temperature increases, while (d) and (e) should become more inefficient due to thermal quenching of the activated species.

From the flow-rate dependence at atmospheric pressure, as opposed to the apparent flow-rate independence at pressures in the millimeter region, it appears as though the reaction is being limited by process (a) at atmospheric pressure. If this is so, then the observed temperature effects at this pressure are probably associated with the temperature dependence of this process. However, at lower pressures, process (a) apparently proceeds rapidly in comparison to the other processes, and thus it is probable that at these pressures the observed temperature dependence of the system would be lower.

In terms of the proposed package, it appears that the useful range of operation extends at least down to -20°C and up to 50°C .

There is no reason to suppose there will be an abrupt "cut-off" in response at some arbitrary temperature, and it is therefore reasonable to assume that the system will maintain adequate sensitivity to ozone over a range of at least 50°C above and below room temperature.

Although the response of the system increases with temperature, it should be noted that the thermal decomposition of ozone becomes increasingly rapid at temperatures above 100°C. Therefore, if the package becomes much warmer than this, most of the ozone would probably be destroyed at the walls of the apparatus before reaching the chemiluminescent disc. In this case, meaningful ozone measurements could not be made, regardless of the temperature-dependence of the disc.

If the expected disc temperature is very much lower than -20°C, the loss in sensitivity may present a problem. However, this could be easily overcome by incorporating a means of electrically heating the disc to a more reasonable temperature. As the mass of the disc (and thus its heat capacity) can be made extremely small if desired, this should require only a nominal amount of power.

Because of the variation in measured temperature coefficients, it appears that, as with disc sensitivity, a pre-flight temperature calibration of the actual unit to be flown would be desirable.

D. Sterilization of Components

The fact that the chemiluminescent discs withstood treatment at 150°C for 24 hours is extremely encouraging, as these had been considered the "weakest link" in the system with respect to sterilization. The only restriction appears to be that oxygen be excluded during the sterilization process. Most of the other electronic and mechanical components should be relatively unaffected by this treatment. Indeed, since the readout circuitry for the final package are not yet decided upon, the only "essential" components which must be considered are the discs, photomultiplier, reaction cell, pump, and gas flow lines.

The lucite reaction cell used in the present sonde is obviously inappropriate for a high-temperature environment. However, this could be replaced with any one of a number of other materials inert to ozone such as stainless steel, or if weight is an important consideration (as it was in the balloon-sonde) a high-temperature plastic such as teflon. The teflon gas flow lines presently being used, together with the silicone RTV "potting," should present no problem when heated.

The neoprene rubber bellows would probably withstand the sterilization treatment. However, it seems desirable to substitute an elastomer having a wider useful temperature range, such as one of the silicone-type rubbers. These rubbers also retain their elasticity and flexibility down to much lower temperatures (-90°C).

Conversations with the manufacturer of the pump motor and assembly (Brailsford and Co.) indicate that the development of a unit which will operate under the environmental conditions specified is well within their capability, and that they are willing to accept a development contract of this nature.

The two high-temperature photomultipliers which have been tested did not appear to have as high a sensitivity as the Dumont tubes presently in use. However, according to the published specifications, there is no reason why this should have been so. It is felt that their response can probably be improved by more closely tailoring the reaction cell and disc size and placement to the particular tube, an aspect which was not fully pursued in the brief A-B comparisons described in this report. As has been noted, even tubes of the same type differ in cathode sensitivity, dark current, gain, etc. Therefore, if necessary, a selection procedure could be instituted to pick optimum tubes from production runs. With the limited funds available nothing of this sort could be attempted during this phase of the work.

The associated electronics are not highly complex, and no problem is foreseen in designing appropriate circuitry employing "approved" high-temperature components.

In summary then, the chemiluminescent discs are not adversely affected by sterilization, and all other components, both mechanical and electronic, can be made to withstand this treatment by present state-of-the-art technology.

E. Sensitivity

The sensitivity of the system to ozone is most properly expressed in terms of $\mu\text{g O}_3/\text{minute}$, rather than $\mu\text{g O}_3/\text{liter}$. This is because, as explained above, the system actually directly measures ozone flux through the cell, and not ozone concentration.

With the Dumont tubes, typical discs have given signals of 1-5 volts at concentrations of $0.1 \mu\text{g O}_3/\text{liter}$, and a flow rate of 300 cc/min (Flux = $0.03 \mu\text{g O}_3/\text{min}$). The high voltage applied to the tube was 1250 VDC, and the signal was measured across a 22 M anode resistor. With no ozone present, the background or "dark current" signal was approximately 0.02 - 0.04 volts. Thus it is quite possible to measure ozone fluxes at least one order of magnitude (and possibly two) lower than this, with the signal remaining well out of the "noise" region. At a pumping speed of 300 cc/min, this would correspond to concentrations of $0.01 - 0.001 \mu\text{g O}_3/\text{liter}$. Higher pumping speeds would make the sensitivity proportionately higher. (With the restriction that excessively high speeds would probably lead to some non-linearity, due to low residence times in the reaction cell.)

V. Summary

An investigation was carried out to determine the feasibility of a chemiluminescent detection system (rhodamine-B on silica gel) for use in measurement of ozone (and/or oxygen) in the Martian atmosphere.

Results indicate that such a device works well at pressures in the millimeter region, and provides a linear measurement of the mass flow rate of ozone through the instrument. Usable signals should be obtained at levels as low as 10^{-9} to 10^{-10} grams of ozone per minute.

Preparation of sensitive chemiluminescent discs is relatively simple and convenient. Once prepared, storage under anhydrous conditions is highly desirable.

If oxygen is excluded, the chemiluminescent discs are not affected by heating to 150°C for 24 hours. Thus, they will withstand pre-flight sterilization procedures.

Storage of discs under anhydrous conditions for about 3 months resulted in no deterioration of sensitivity. In fact, it generally improved their response, and tended to minimize sensitivity variations between the discs.

Temperature coefficients of freshly prepared discs are variable, probably due to varying moisture contents. However, dry storage also improves their behavior in this respect.

Disc sensitivities are approximately linear with temperature over the range -20°C to $+50^{\circ}\text{C}$ ($\sim 1\%$ per $^{\circ}\text{C}$ at 20°C). The useful temperature range of the instrument should extend over a range of at least -30°C to $+70^{\circ}\text{C}$.

Two different high-temperature photomultiplier tubes were evaluated, an ASCOP 543D and a CBS CL-1158. Neither gave as high a sensitivity as the Dumont 6467 normally used with the system. However it is believed that comparable sensitivities can be achieved by further development work.

No factor is presently anticipated, either in pre-flight procedures or during operation, which would render the chemiluminescent system undesirable for the contemplated mission.

DETERMINATION OF OXYGEN

I. Introduction

The extremely high sensitivity of the chemiluminescent method for detection of ozone suggests a possible indirect scheme for detection and measurement of molecular oxygen. If an oxygen-containing gas is irradiated by ultra-violet light, some of the oxygen will be converted to ozone (by the same process utilized in the ozone generators described in the previous section). The resultant ozone could then be detected by its chemiluminescent reaction, and ought to be directly related to the original oxygen content of the gas.

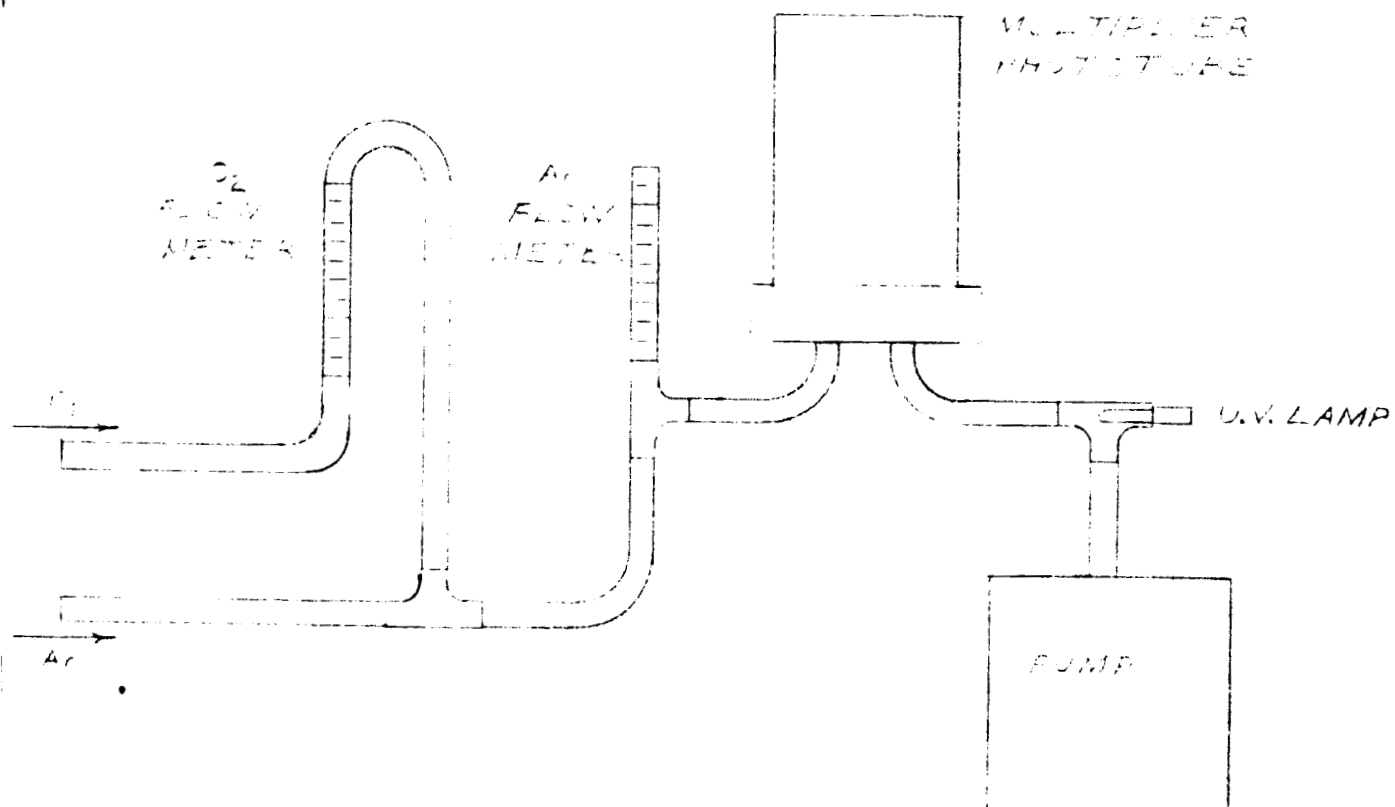
Only a limited amount of effort was devoted to this topic. However, enough information has been elucidated to serve as a reasonable guide to the phenomena encountered, and to point the way to further experimental work.

II. Experimental

A. Atmospheric Pressure

The initial work was done at atmospheric pressure in the system depicted in Fig. 18 . Various concentrations of oxygen in argon were established by manipulating the flow rates of each as shown. A portion of this flowing mixture was periodically aspirated by the reciprocating bellows pump, so that the gas parcel passed over the "Pen-Ray" lamp and thence immediately into the reaction cell for ozone analysis. It was found to be

FIGURE 18



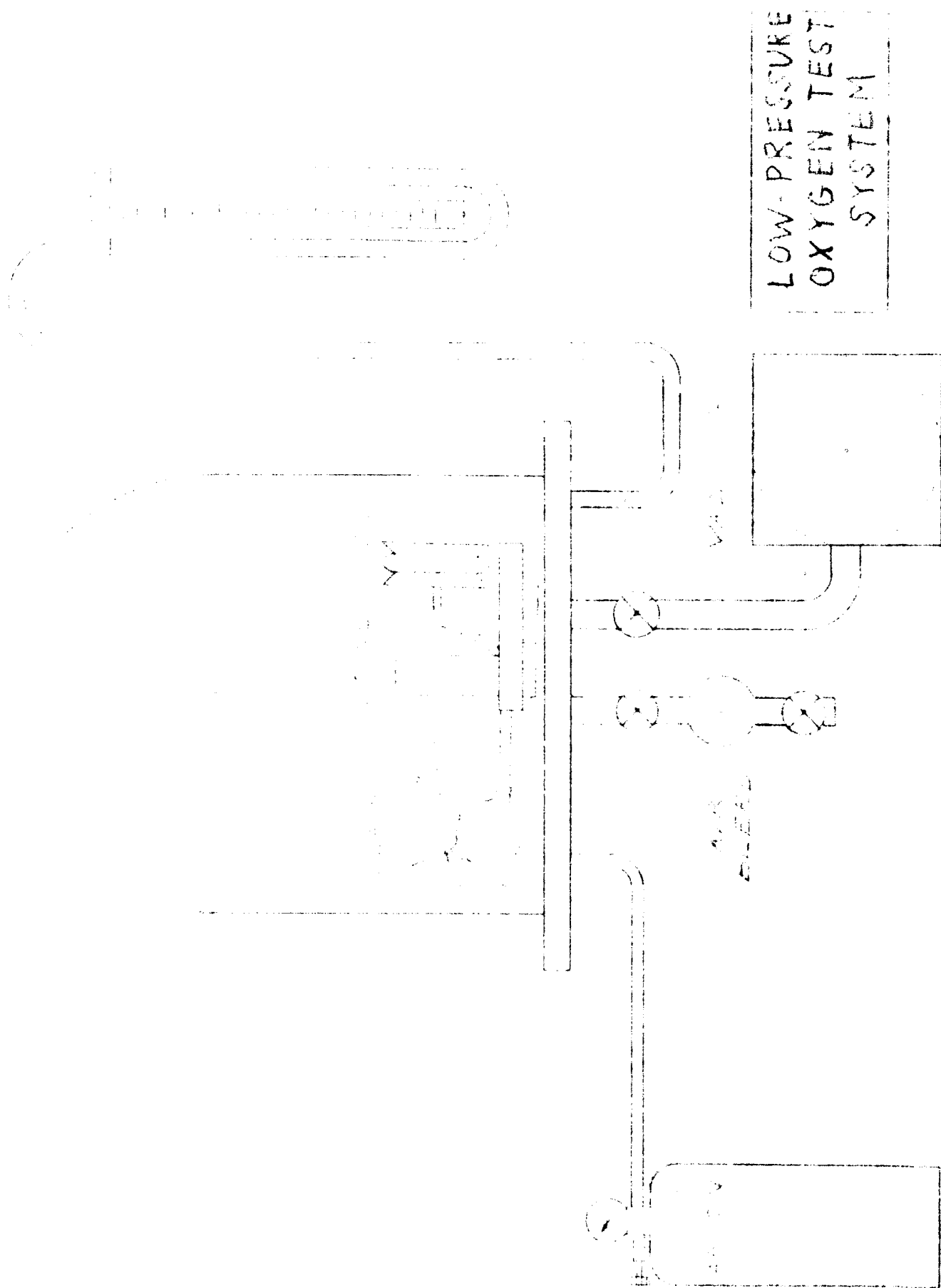
OXYGEN TEST
SYSTEM

necessary to use a dynamic system of this sort, rather than a static gas mixture, as diffusion of atmospheric oxygen into the system, despite many precautions, always occurred unless all gases were continually flowing and under a slight positive pressure. The argon used was Linde High-Purity (99.995%), and this was found suitable for most work, although a slight background signal was always obtained. Whether this was due to residual traces of oxygen in the argon, or to diffusion from the atmosphere, was not clearly established. Nitrogen of high enough purity to make meaningful measurements was not available soon enough to include in this work. Toward the end of the project, pre-calibrated oxygen-argon mixtures (Matheson Co.) became available, and these were used to some extent.

B. Low Pressure

For testing this concept at low pressures, the system shown in Fig. 19 was constructed. At this time a prototype ozone sonde of the type described in the appendix became available, and it was decided to use this unit, rather than the experimental reaction cell, as the ozone sensor. A small glass bulb (about 100 cc) containing a Pen-Ray Lamp, was affixed to the intake of the sonde and the entire unit placed in a large bell-jar. The jar was then evacuated, and various oxygen-argon mixtures at different pressures were established by bleeding the two gases into the bell-jar. Because of the large volume of the bell-jar, it was quite uneconomic to use a dynamic system, and indeed, it was found that atmospheric diffusion into the jar was negligible. This, however, was not true of the argon line outside the bell-jar, and it was

FIGURE 19



necessary to flush this line vigorously before adding argon to the jar, especially if the gas had not been flowing for some time.

III. Results

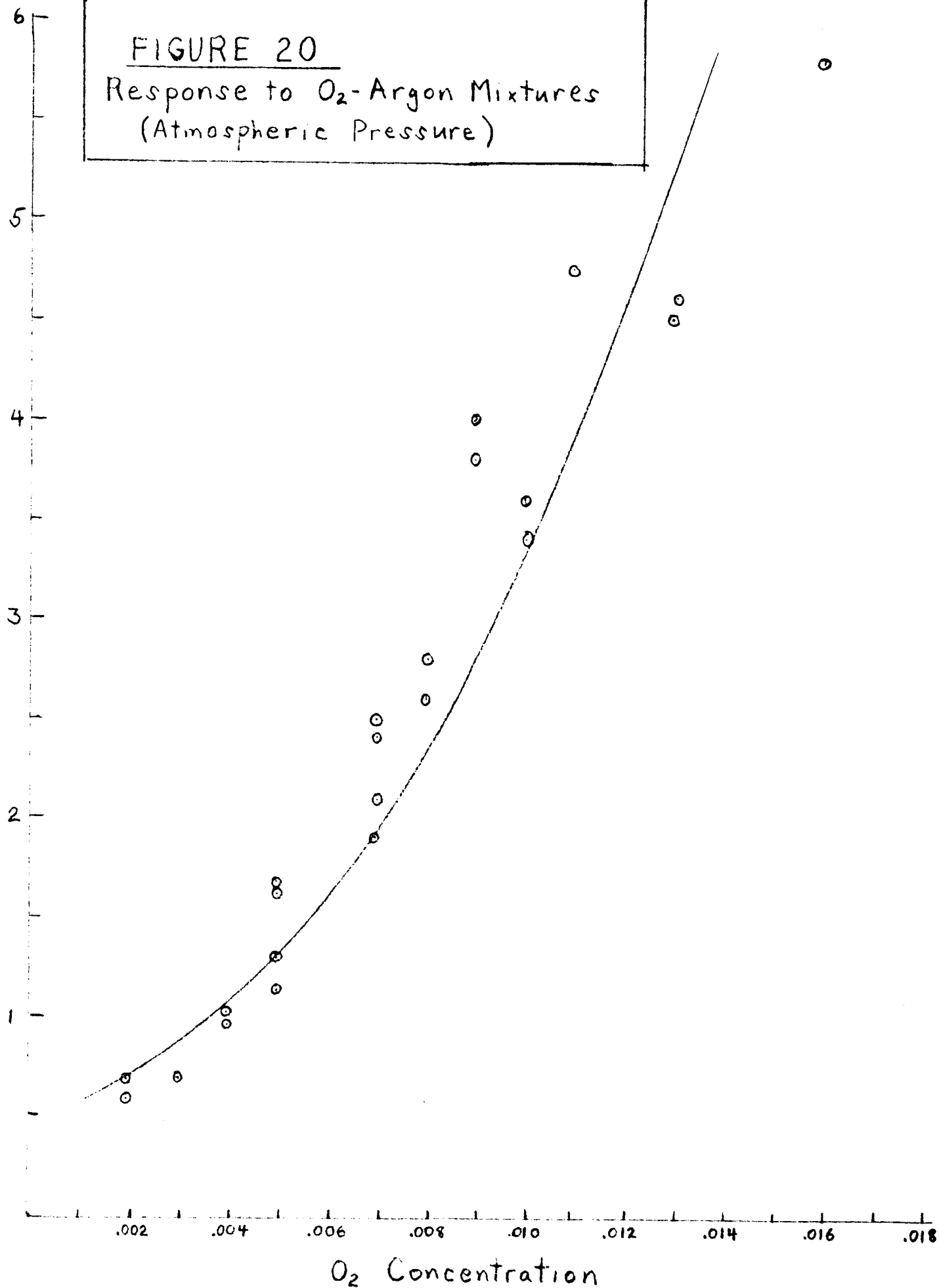
A. Atmospheric Pressure

Typical results from the work at atmospheric pressure are shown in Fig. 20 . The oxygen concentrations shown are calculated from the flow rates as read by the flow meters, and are necessarily crude, due to the low flow rates of oxygen involved. The shape of the curve, however, with a slight positive curvature, is quite typical. It was later found that the design used for most of the atmospheric pressure work (Fig. 18) was not the most efficient, and that greater sensitivity was achieved by substituting the arrangement used for the low-pressure experiments, i. e. , a small irradiation bulb, followed by the prototype sonde. This might be explained on the basis of: (a) the sonde was more sensitive to ozone than the reaction cell, due to more efficient geometry, both for reaction and optically: (b) the irradiation bulb, which was approximately the same volume as the pump stroke, allowed for some stagnation of the gas in the bulb when the pump stroke reached bottom, thus increasing the effective residence time of the gas in the vicinity of the lamp. Using the pre-mixed gases referred to above, it was found that this arrangement could readily detect 0.01% O_2 in argon at atmospheric pressure. Because of the low oxygen concentration involved, atmospheric leakage was an extreme problem in this case, despite all precautions. As this "leakage

FIGURE 20

Response to O_2 -Argon Mixtures
(Atmospheric Pressure)

Gross Signal (Volts)



background" varied it was not possible to obtain reproducible signals, although it was apparent that the signal from the 0.01% O₂ was several times the background signal.

B. Low Pressure

The low pressure experiments were performed to determine (a) the dependence of the signal on pressure at constant oxygen concentration, (b) the dependence on oxygen concentration at constant pressure. The pressure dependence was investigated by filling the bell jar to various pressures with argon, and then leaking in a fixed amount of oxygen (air). If the argon pressure was high compared with the oxygen pressure, the oxygen dependence at this pressure could be investigated by repeatedly leaking in fixed amounts of oxygen. The results of the complete series of experiments are tabulated in Tables I and II and plotted in Figs. 21 and 22, respectively. It will be noted that the signal is highly dependent on the total pressure in the region of interest (10-100 mm), becoming relatively pressure-independent at about 200 mm. At 73 mm, 100 mm and 200 mm, the oxygen dependence appears to be exponential ($S = K [O_2]^{1.6}$). At the lower pressures (0 mm and 10 mm) admission of oxygen into the system changed not only the oxygen concentration, but also the total pressure, and the relationship is therefore more complex. Thus although still exponential, the exponents are higher.

C. Comparison of Ultra-Violet Lamps

During the course of this work, three different lamp models, all produced by UV Products, Inc., were tested, in the apparatus

FIGURE 21

SIGNAL VS TOTAL PRESSURE (AVERAGE)
 @ CONSTANT PARTIAL PRESSURE OF AIR (15 mm.)

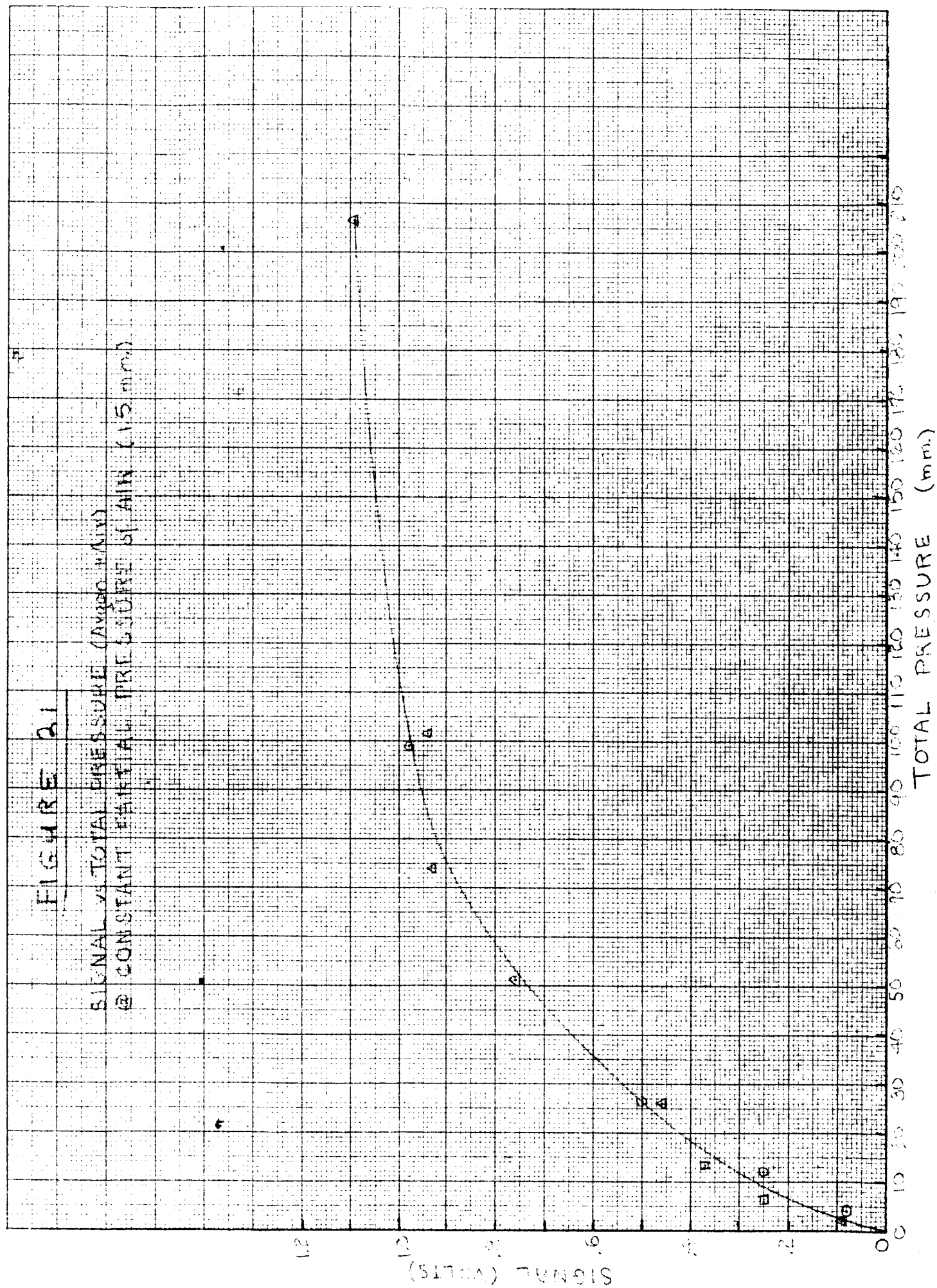
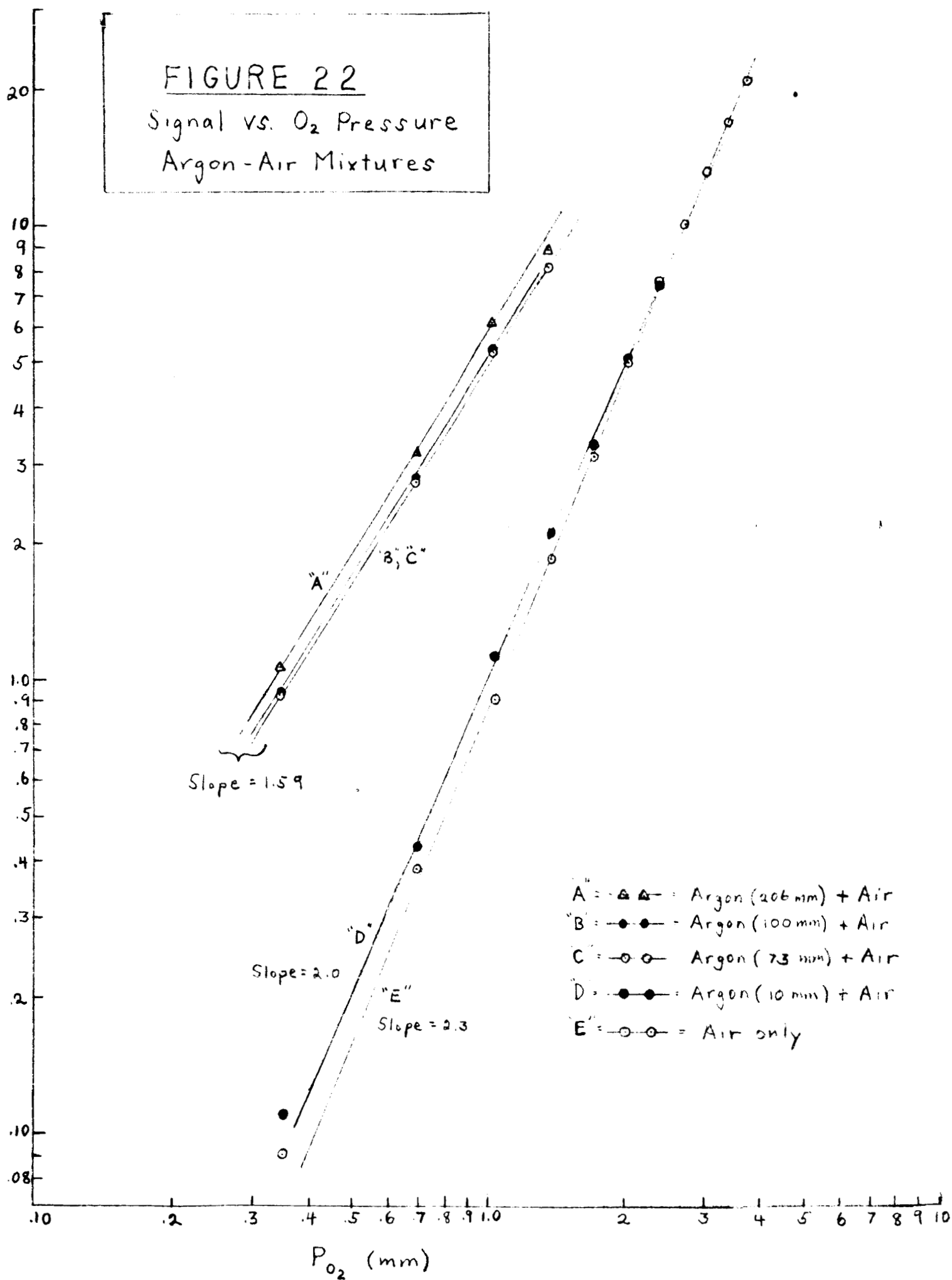


FIGURE 22

Signal vs. O_2 Pressure
Argon-Air Mixtures

SIGNAL (VOLTS)



described above in order to obtain a rough comparison as to ozone-production efficiency. The first lamp was the "standard" 11SC-1, with which all the preceding data was obtained. This lamp is about 5 cm long (excluding base) and about 6 mm in diameter. It operates at 270 volts AC (800 volts to start), drawing about 5 watts. Another lamp tested was the "miniature" 22SC-3, about $1\frac{1}{8}$ long and 4 mm in diameter. This lamp operates at 270 volts, drawing 3 watts. As a result of correspondence with the manufacturer, we also obtained a lamp having a very thin (~ 0.2) quartz wall. It was hoped that this would increase the efficiency of the lamp by absorbing less of the UV wavelengths responsible for oxygen dissociation. This last lamp was a modified 11SC-2, the discharge column being semi-spherical, about 7 mm in diameter.

Of the three lamps tested, the larger 11SC-1 was by far the most efficient, the other two producing about one half as much ozone.

TABLE I

Signal Due to 1.5 mm Air at Various Argon Pressures

<u>P_A (mm)</u>	<u>P_{air} (mm)</u>	<u>P_{O₂} (mm)</u>	<u>P_{total} (mm)</u>	<u>Net Signal (volts)</u>	<u>O₂ Signal (volts)</u>
0	1.5	0.3	1.5	0.09	0.09
2	0	0	2	0	
2	1.5	0.3	3.5	0.08	0.08
10	0	0	10	0.05	
10	1.5	0.3	11.5	0.30	0.25
25	0	0	25	0.10	
25	1.5	0.3	26.5	0.60	0.50
98	0	0	98	0.27	
98	1.5	0.3	99.5	1.25	0.98
5	0	0.3	5	0	
5	1.5	0.3	6.5	0.25	0.25
12	0	0	12	0.13	
12	1.5	0.3	13.5	0.50	0.37
24	0	0	24	0.09	
24	1.5	0.3	25.5	0.55	0.46
49	0	0	49	0.12	
49	1.5	0.3	50.5	0.88	0.76
73	0	0	73	0.12	
73	1.5	0.3	74.5	1.05	0.93
100	0	0	100	0.16	
100	1.5	0.3	101.5	1.10	0.94
206	0	0	206	0.16	
206	1.5	0.3	207.5	1.25	1.09

TABLE II
Signal Due to Air At Various Total Pressure

P_A (mm)	P_{air} (mm)	P_{O_2} (mm)	P_{total} (mm)	Net Signal (volts)	O_2 Signal (volts)
73	0	0	73.0	0.12	0
"	1.75	0.35	74.75	1.05	0.93
"	3.5	0.70	76.5	2.85	2.73
"	5.25	1.05	78.25	5.35	5.23
"	7.0	1.40	80.0	8.25	8.13
100	0	0	100.0	0.16	0
"	1.75	0.35	101.75	1.10	0.94
"	3.5	0.70	103.5	2.97	2.81
"	5.25	1.05	105.25	5.65	5.49
206	0	0	206.0	0.16	0
"	1.75	0.35	207.75	1.25	1.09
"	3.5	0.70	209.5	3.35	3.19
"	5.25	1.05	211.25	6.25	6.09
"	7.0	1.40	213.0	9.00	8.84
10	0	0	10.0	0.04	0
"	1.75	0.35	11.75	0.15	0.11
"	3.5	0.70	13.5	0.47	0.43
"	5.25	1.05	15.25	1.16	1.12
"	7.0	1.40	17.0	2.15	2.11
"	8.75	1.75	18.75	3.35	3.31
"	10.5	2.10	20.5	5.10	5.06
"	12.25	2.45	22.5	7.45	7.41

TABLE II (Cont'd)

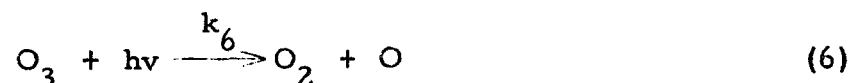
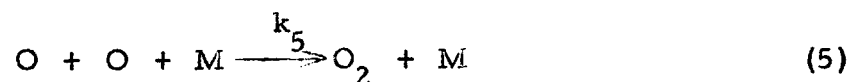
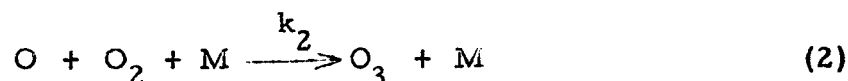
<u>P_A (mm)</u>	<u>P_{air} (mm)</u>	<u>P_{O₂} (mm)</u>	<u>P_{total} (mm)</u>	<u>Net Signal (volts)</u>	<u>O₂ Signal (volts)</u>
0	0	0	0	0	0
"	1.75	0.35	1.75	0.09	0.09
"	3.5	0.70	3.5	0.38	0.38
"	5.25	1.05	5.25	0.90	0.90
"	7.0	1.40	7.0	1.85	1.85
"	8.75	1.75	8.75	3.10	3.10
"	10.5	2.10	10.5	5.0	5.0
"	12.25	2.45	12.25	7.4	7.4
"	14.0	2.80	14.0	10.0	10.0
"	15.75	3.15	15.75	13.1	13.1
"	17.50	3.50	17.5	16.9	16.9
"	19.25	3.85	19.25	20.8	20.8

IV. Discussion and Conclusions

The results obtained from the preceding experiments are qualitatively in line with what would be expected from theoretical considerations. Both the absolute oxygen concentration and the total pressure should affect the amount of ozone produced.

Consider the kinetic processes which occur in a parcel of oxygen-containing gas which is exposed to ultraviolet radiation for a period of time t_1 , then is removed from the UV source and travels down a tube for time t_2 , until it enters the reaction cell where the ozone content is measured.

The equations governing the system in question are:



where M = third body

In the irradiation zone, we shall assume that the important processes affecting the $[O]$ concentration are (1), (2) and (3); while the $[O_3]$ concentration is determined essentially by (2):

$$\begin{aligned}\frac{d[O]}{dt_1} &= 2k_1 [O_2] - k_2 [O] [O_2] [M] - k_3 [O] \\ &= 2k_1 [O_2] - [O] (k_2 [O_2] [M] + k_3)\end{aligned}$$

Integrating over time t_1 :

$$[O] = \frac{2k_1 [O_2]}{k_2 [O_2] [M] + k_3} (1 - e^{-(k_2 [O_2] [M] + k_3)t_1})$$

Also

$$\begin{aligned}\frac{d[O_3]}{dt_1} &= k_2 [O_2] [M] [O] \\ &= \frac{2k_1 k_2 [O_2]^2 [M]}{k_2 [O_2] [M] + k_3} (1 - e^{-(k_2 [O_2] [M] + k_3)t_1})\end{aligned}$$

Integrating:

$$[O_3]_1 = \frac{2k_1 k_2 [O_2]^2 [M]}{k_2 [O_2] [M] + k_3} \left\{ t_1 + \frac{1}{k_2 [O_2] [M] + k_3} (e^{-(k_2 [O_2] [M] + k_3) t_1} - 1) \right\}$$

Upon leaving the irradiation zone:

$$\begin{aligned} \frac{d[O]}{dt_2} &= -k_2 [O_2] [M] [O] - k_3 [O] \\ &= -[O] (k_2 [O_2] [M] + k_3) \end{aligned}$$

Integrating:

$$[O] = [O]_1 e^{-(k_2 [O_2] [M] + k_3) t_2}$$

Also

$$\begin{aligned} \frac{d[O_3]}{dt_2} &= k_3 [O_2] [M] [O] \\ &= k_2 [O_2] [M] [O]_1 e^{-(k_2 [O_2] [M] + k_3) t_2} \\ &= \frac{2k_1 k_2 [O_2]^2 [M]}{k_2 [O_2] [M] + k_3} (1 - e^{-(k_2 [O_2] [M] + k_3) t_1}) e^{-(k_2 [O_2] [M] + k_3) t_2} \end{aligned}$$

Integrating

$$[O_3]_2 = [O_3]_1 + \frac{2k_1 k_2 [O_2]^2 [M]}{(k_2 [O_2] [M] + k_3)^2} (1 - e^{-(k_2 [O_2] [M] + k_3)t_1}) (1 - e^{-(k_2 [O_2] [M] + k_3)t_2})$$

$$[O_3]_2 = \frac{2k_1 k_2 [O_2]^2 [M]}{(k_2 [O_2] [M] + k_3)^2} \left\{ (k_2 [O_2] [M] + k_3)t_1 + e^{-(k_2 [O_2] [M] + k_3)t_2} (e^{-(k_2 [O_2] [M] + k_3)t_1} - 1) \right\}$$

Note that at "high" values of the exponents $(k_2 [O_2] [M] + k_3)t$, the expression simplifies to:

$$[O_3]_2 = \frac{2k_1 k_2 [O_2]^2 [M]}{k_2 [O_2] [M] + k_3} t_1$$

Thus the dependence of signal on total pressure $[M]$ appears reasonable (Fig. 21). Depending on the relative values of the two terms in the denominator, the resultant ozone concentration should be proportional, in the extreme cases, to either the first or second power of the oxygen concentration. The 1.6 power dependence on $[O_2]$ found experimentally at constant $[M]$, is therefore not unreasonable.

In the cases where the initial argon pressures are low (0 and 10 mm) the addition of air to the system appreciably changes the total pressure (i. e. , $[M] \approx 5 [O_2]$). Therefore the expression becomes

$$[O_3]_2 = \frac{10 k_1 k_2 [O_2]^3}{5k_2 [O_2]^2 + k_3}$$

Thus the $[O_2]$ dependence ought to be between first and third power, again depending on the magnitude of the terms in the denominator. The 2.0 and 2.3 power dependencies which were found are therefore qualitatively explainable on this basis.

With respect to development of a workable instrument for oxygen detection, the dependence of the signal on total pressure in the region of interest (10 - 100 mm) is unfortunate. There is also undoubtedly a dependence of k_2 on the particular "third body" $[M]$, which is present, although the third-body efficiencies of N_2 and A, might well be similar.

The low absolute sensitivity at the lower pressures is also disappointing. However, it is not known how efficient the UV lamp is in dissociating oxygen, and it might be possible to improve this process (k_1) by selection of a much more efficient ultraviolet source.

V. Summary

The measurement of oxygen by the indirect procedure of UV-irradiation followed by ozone detection was briefly investigated. The response of the system is dependent on both the oxygen concentration and the total pressure. High sensitivities were achieved at atmospheric pressure (detection limit $\sim 0.01\%$ O_2). However, at pressures in the range 10 - 100 mm the low total pressure decreases the sensitivity of the method. More efficient dissociation of the oxygen than is currently achieved by the UV lamp would raise the overall sensitivity correspondingly.

APPENDIX

A. The Ozone Sonde

The ozone sonde, in its configuration for balloon-borne high-altitude measurements, operates in the following manner:

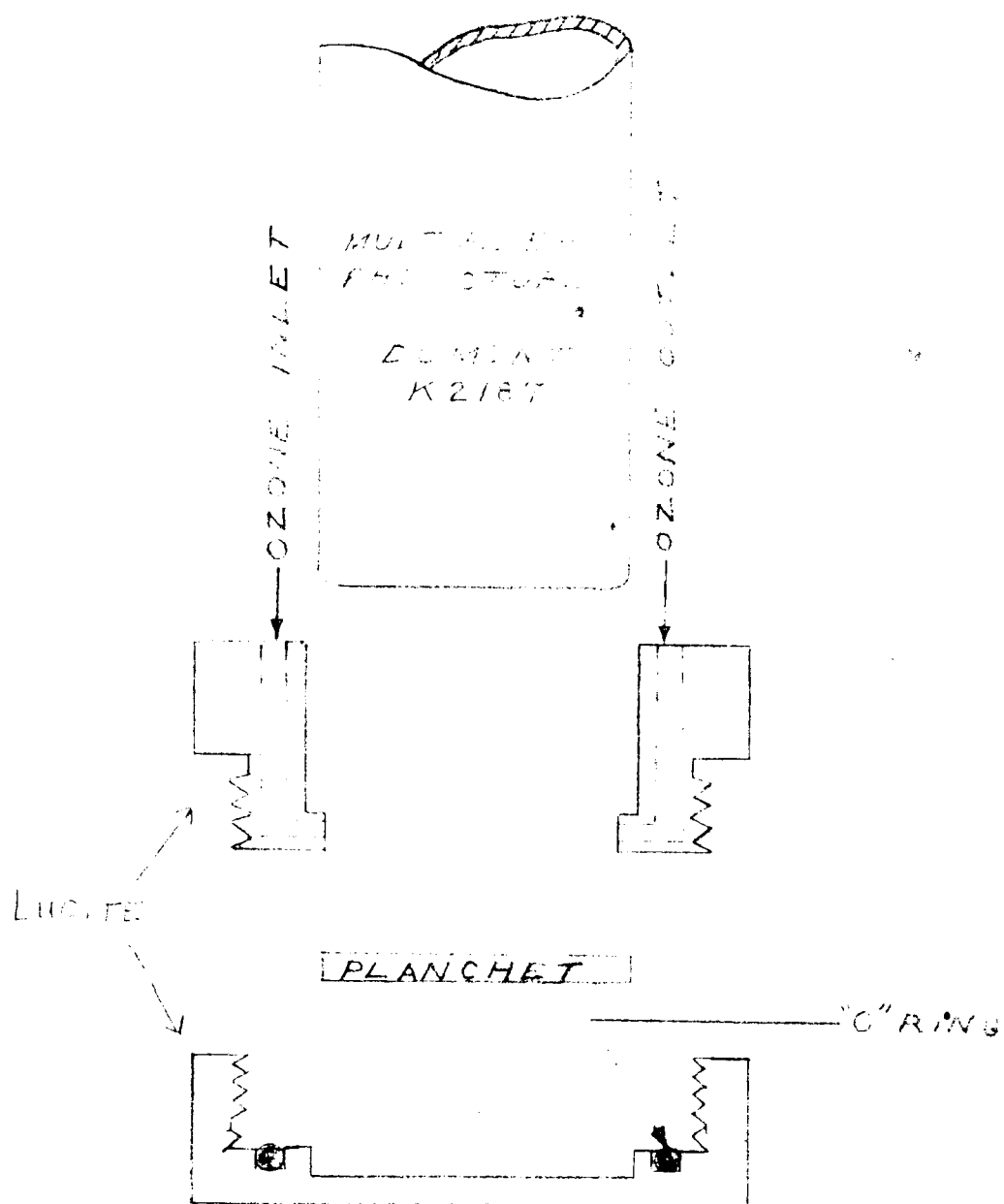
1. Mechanical

The air to be sampled is aspirated through a 1/8" teflon intake tube. This tube is coiled around the Dumont K 2187 photomultiplier (same as Model 6467, but with bare wire leads), and enters the lucite reaction chamber at the head of the phototube. Here it passes over the chemiluminescent disc, and exits via another teflon tube, which is connected directly to the reciprocating bellows pump.

The pump assembly (Brailsford & Co., Inc., Rye, N. Y.) is powered by a geared-down 6-volt DC motor, which by means of an eccentrically mounted cam, expands and compresses the neoprene bellows once every thirty seconds. The fully expanded volume of the bellows is approximately 75 cc. Thus, the average flow rate of gas during the 15 second intake stroke is about 300 cc/min.

The lucite reaction chamber (Fig. 15) is a two-piece affair. One portion, containing the entrance and exit tubes is affixed to the end of the photomultiplier. The other portion

FIGURE 15



OZONE SONDE
REACTION CHAMBER

containing the chemiluminescent disc, screws onto the former, making an airtight seal against the "O" ring. This design affords convenient removal and replacement of the chemiluminescent disc.

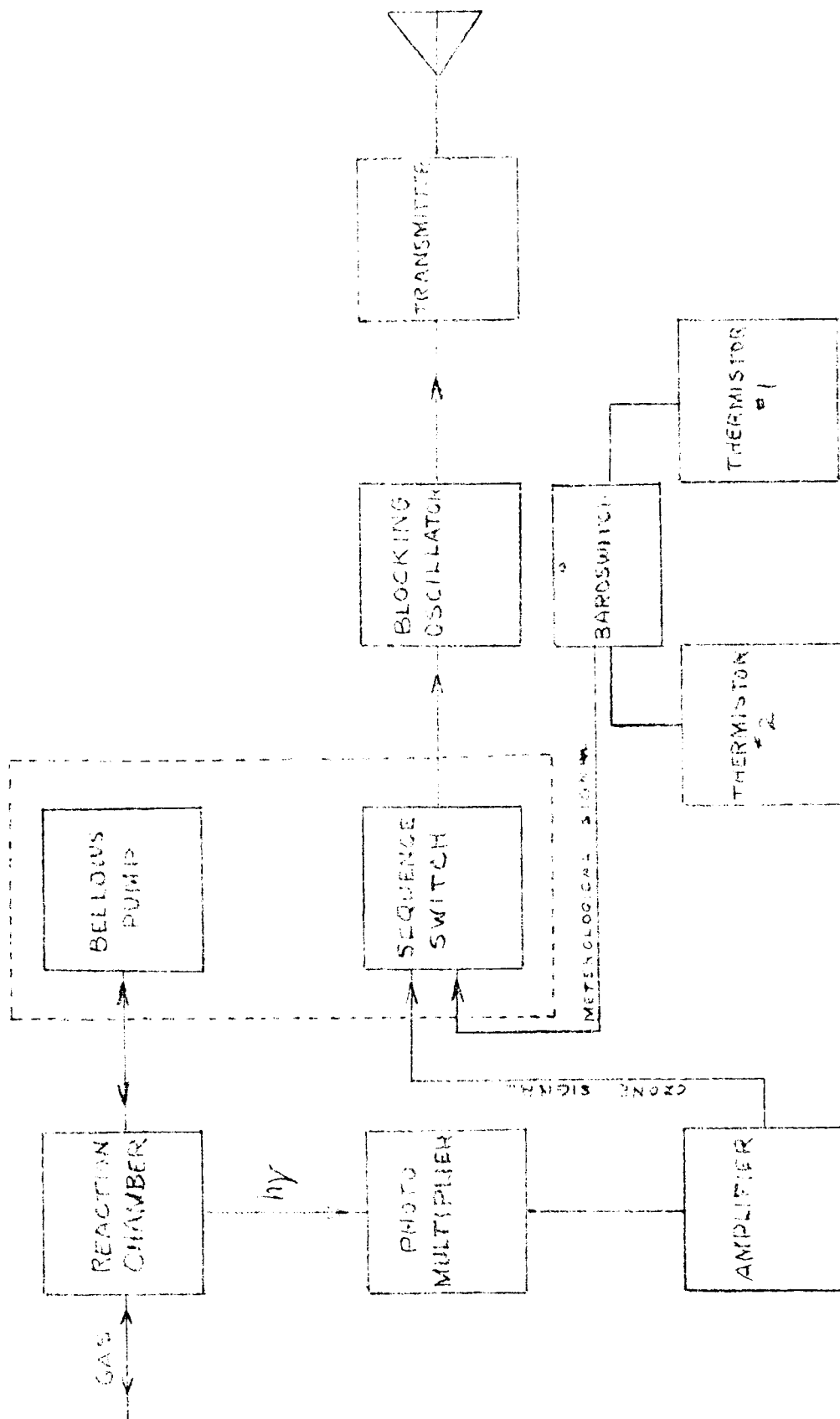
The photomultiplier, entrance and exit tubes, and attached portion of the reaction chamber, are all sealed in a 2" cardboard mailing tube, using black Silastic RTV silicone rubber (Dow Corning Corp.). This increases the rigidity of the unit, and also suppresses any possible light leaks.

2. Electronic

Figure 16 is a block diagram of the components of the complete system, including AMT4-B radiosonde transmitter and associated meteorological sensors. The shaft which operates the bellows pump also operates a rotary sequence switch so that the normal "meteorological" channel is interrupted twice in each revolution; once when the pump is completely compressed (ozone "zero" reference) and once when the pump is expanding and aspirating air into the reaction chamber (ozone signal).

Figures 17A and 17B are circuit diagrams for the sonde, excluding the AMT4-B. The photomultiplier tube is followed by one stage of DC coupled amplification employing a CK 5676 subminiature pentode. The photomultiplier high voltage supply employs a Texas Instruments 2N 1039 silicon transistor in a conventional blocking oscillator type circuit. The generated

FIGURE 16



BLOCK DIAGRAM OF
OZONE SONDE
AND AUT-4-B
TRANSMITTER

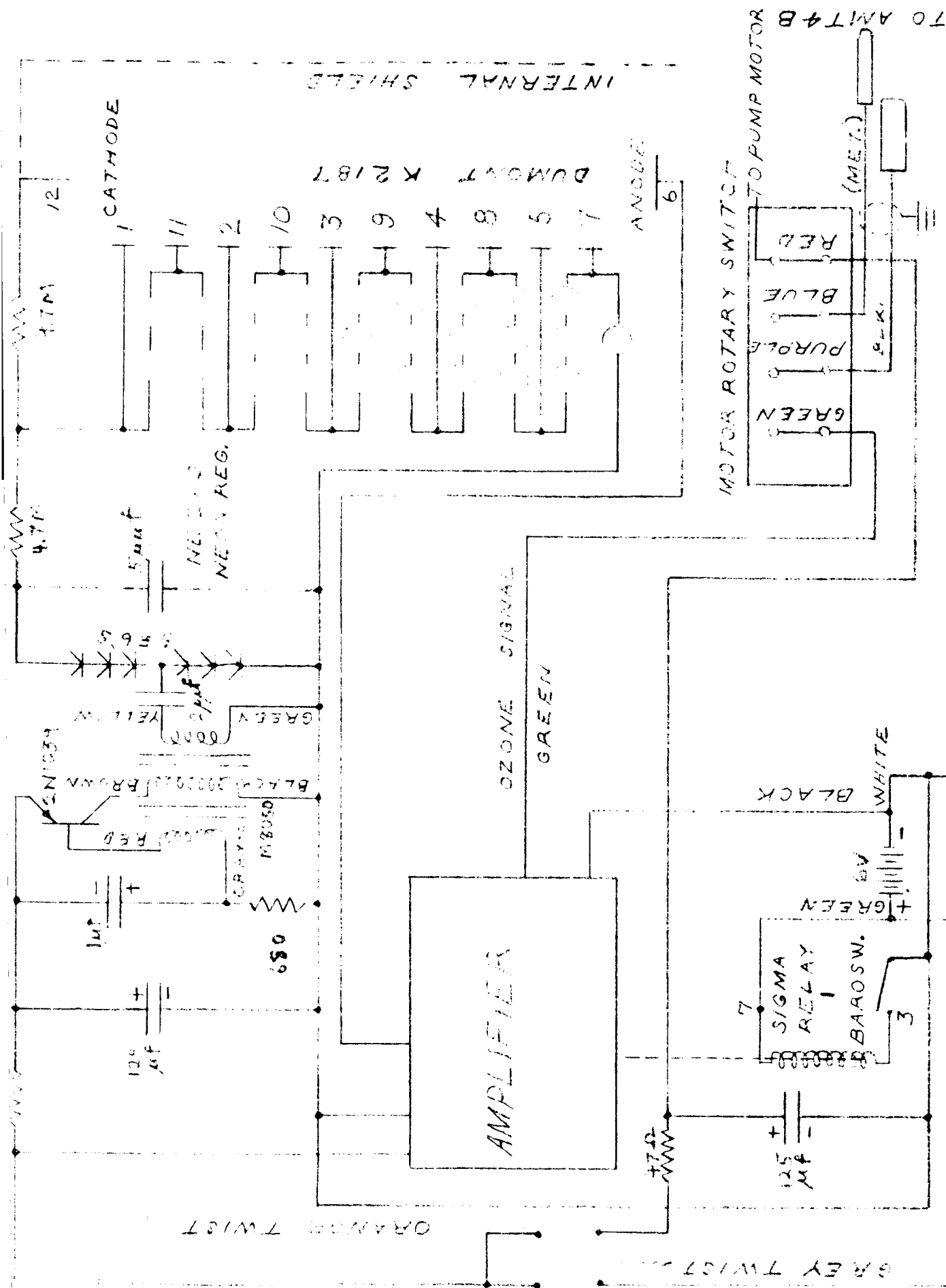


FIGURE 17A

ZONE SONDE
SCHEMATIC

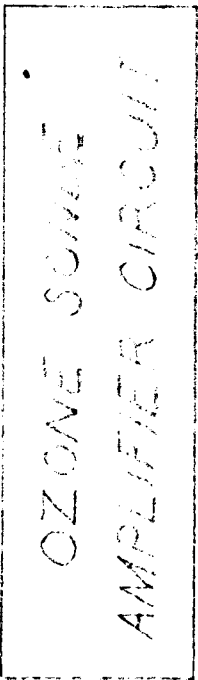


FIGURE 17B

frequency is about 500 cps, and the voltage is stepped up to 1600 V, rectified and filtered. The DC voltage applied across the phototube is about 1500 VDC. A series of NE 2AS neon lamps serves as a voltage regulated bleeder chain for the phototube. The unit is powered by a set of four 1.5 V manganese-alkaline cells, series connected. The +110 VDC for the pentode is supplied by the AMT4B transmitter battery.

The light emitted by the chemiluminescent disc is sensed and amplified by the photomultiplier tube. The phototube anode current passes through R_{1A} , R_{1B} , R_{1C} , a ganged combination of potentiometers (in series) located in the anode circuit. The useful signal appears as a negative voltage developed across this resistance which is fed to the control grid of the CK 5676. This tube is normally biased conducting for zero signal. Consequently the plate current moves toward cutoff with increasing negative signals applied to the grid. This causes the plate voltage to rise toward +110VDC as the increasing signal cuts off the plate current. This positive-going DC voltage is coupled to the grid of the blocking oscillator tube in the AMT4-B transmitter, through R_2 , R_3 and the rotary sequence switch.

This unit has provision for scale switching at preselected altitudes. The least sensitive range is the normal one, in which Relay 1, unenergized, connects the arm of R_{1C} to the grid of the CK 5676. Thus the amplifier input is only one tenth the actual voltage developed across the anode resistor. The most sensitive

range is normally actuated at 80,000 - 90,000 feet, as the ambient ozone concentration rapidly decreases with altitude above this point. Switching is effected by the baroswitch, which actuates Relay 1, thus connecting the CK 5676 grid to R_{1A} , increasing the effective phototube anode resistance by a factor of ten.